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THE CHEMICAL ACTION OF ULTRAVIOLET RAYS

BY

CARLETON ELLIS

AND

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Assisted by Norris Boehmer

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*

19 EAST 24TH STREET, NEW YORK, U. S. A.

1925

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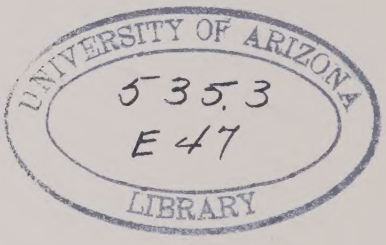

Printed in the United States of America by
J. J. LITTLE AND IVES COMPANY, NEW YORK

Preface.

In 1917 a representative of the publication then known as the Chemical Engineer visited the laboratory and asked for a contribution on some chemical subject. Investigations being in progress on the effect of ultraviolet radiation and on its possible commercial applications led the authors of the present volume to contribute data on the subject to the columns of that journal. These articles extended over the period 1917 and 1918.

Requests for reprints of these articles came to hand in such numbers that the authors concluded there existed a demand for a treatise on the subject of ultraviolet radiation and hence undertook the revision of the material collected on the subject up to that time. The protracted absence of one of the authors in Japan retarded the work for a considerable period.

The publication of each noteworthy discovery involving ultraviolet radiation brought further requests for reprints of the series of articles.

The correspondence which ensued indicated that those making inquiry for reprints were interested in different phases of the action of ultraviolet rays. The inauguration and growth of the dye industry in this country made imperative the development of methods for ascertaining the fastness of dyes; in this, ultraviolet radiation proved an important consideration. The bleaching of oils occupied the attention of others. Those interested in the more sensational side wished, for example, to confirm the alleged report of ultraviolet radiation changing mercury to gold or to determine if the so-called death ray discussed from time to time by the daily press involved the application of ultraviolet rays in some form. Interest in ultraviolet radiation has been stimulated by the work of a group of British chemists on the synthesis, through the action of ultraviolet rays, of carbohydrates and proteins. Popular interest in ultraviolet has been enhanced through the observation that this form of radiation is capable of creating vitamins or their equivalents in certain food products normally deficient in these essential components. The remedial effects of ultraviolet in rickets and other diseases connected with a deficiency of vitamins have attracted the attention of the whole medical profession. In the latter field there has been much empiricism concerned with the application of ultraviolet rays. Chapters are included on therapeutic applications and the biological effects of ultraviolet radiation, which should be of interest to those engaged in medical work.

The chapter relating to the possibilities of making synthetic foods through the action of ultraviolet rays is one which it is hoped will

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prove of value to the considerable number of research chemists now devoting their efforts to a study of this subject.

Ultraviolet radiation represents one more instrumentality available to the chemist in the synthesis and decomposition of substances. It has its limitations as well as its field of applications and respecting the latter the authors believe the following pages quite freely set forth the numerous reactions characterizing this field. The subjects of spark spectra, absorption spectra, phosphorescence, luminescence and photo-electric effects involving radiations within the ultraviolet range are not included herewith as other publications traverse these subjects rather fully in most respects.

From an inspection of the contents it will be evident that it has been the object of the authors to confine the undertaking largely to the more strictly chemical effects of ultraviolet radiation.

Our thanks are due to Mr. P. L. Young, Dr. H. O. Nolan, Mr. P. A. E. Armstrong, Mr. Henry Green, Dr. G. M. Maverick, Mr. D. L. Ferguson, Ellis Foster Company, Cooper Hewitt Electric Company, Hanovia Chemical and Manufacturing Company, Victor X-Ray Corporation, Research Division of the New Jersey Zinc Company, Thomson Research Laboratory of the General Electric Company and others who have furnished us with, or checked any data, considered in connection with the preparation of this volume.

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Chapter I.

Introduction.

NATURE OF ULTRAVIOLET RADIATION.

In the every-day routine of the laboratory the chemist makes constant demand on the domain of physics. He employs heat, cold, electricity and various other physical agencies to facilitate the combination of atoms or rupture of molecules. The agency of light and the field of photolysis, aside from photography, have however received but relatively scant usage in operations on a commercial scale. To be sure, a few photochemical processes of an industrial character, such as the production of benzyl chloride, have had a limited commercial application, but most chemical operations involving the energy of sunlight have been found slow and ineffective. The subject of photochemistry has received a powerful stimulus through the study of ultraviolet radiation and its applications in chemical arts. The number of branches of chemistry in which this radiation has been studied is always a source of surprise to chemists when they first become cognizant of the facts.

The prediction made by Sheppard in his book on photochemistry that "We are only at the beginning of the conscious utilization of the powers of light, as distinct from the unconscious enjoyment of them" may have its fulfilment at a future by no means remote.

For many years past the chemist has realized that all about him, in the growth of vegetation, the rays of sunlight were acting, in some powerful, mysterious and, in fact, quite inexplicable manner, to effectuate reactions which he, in the laboratory, was unable to reproduce. How to capture light rays and put them to work in a manner analogous to that of nature has been a problem for which no definite starting point was recognized. The production of vegetable foodstuffs is fraught with many vicissitudes. The farmer breaks the soil, plants seeds, fertilizes and prays for good weather. When the plants appear they are attacked by insects and smothered by weeds and the utmost vigilance is required to yield a fair crop. The human effort required in the production of foodstuffs is tremendous, the outcome precarious. If the chemist could make use of rays of light to bring about chemical reactions producing the equivalent of vegetable growth, basic foodstuffs might then be created in the vats and kettles of a factory under conditions closely regulated by chemical supervision, instead of having the farmer till the soil, fight off the encroaches of insects and weeds and have his land watered by rains in haphazard fashion. In other

words instead of having the production of foodstuffs carried out under fortuitous conditions, the element of chance would be eliminated by well-controlled chemical operations.

The development of such an idea has been beset with difficulties because there has been no effective source of light available. In plant life the chlorophyll acts in its mysterious way, to bring about the reactions in the plant cells. In recent years two promising developments have pointed the way to further investigations. One of these is the quartz mercury arc lamp giving rise to a ready means of production of ultraviolet rays for experimental purposes and the other is the use of fluorescent bodies which are capable of absorbing light of one wave-length and giving it out as light of a different length.

The availability of sources of ultraviolet rays of this character has led to very many investigations on the use of light of short wave-length in chemical arts and in this volume there has been brought together a fairly complete description of the work carried out in the field.

New types of ultraviolet lamps are being brought on the market (see Chap. 2) and the gradual improvement of these instrumentalities is a source of satisfaction to those who recognize the possibilities of ultraviolet energy. Much however remains to be accomplished in the refinement of apparatus.

Ultraviolet radiation partly owes its exceptional photochemical activity to the circumstance that it is absorbed with relative ease by most substances; including colorless gases and liquids transparent to ordinary light; but this characteristic is also the cause of most of the difficulties which arise in the study of the effects producted by it. Practically all substances are opaque to the extreme ultraviolet rays and the chemical action of these rays is as yet but little known. The discovery of a material of the requisite physical properties which would be transparent to extreme ultraviolet radiation should lead to important developments in the chemical world. The disruptive forces of these extreme rays compare in many ways with those produced by very high temperatures and the possibility of carrying out in the cold, reactions heretofore requiring electric furnace temperatures is at least an interesting topic of speculation to the research chemist.

Before considering in a more detailed way the many applications and effects of ultraviolet rays it may be helpful to review briefly the nature of the radiations involved, and to sketch the history of the work by which our present knowledge was gained.

Every light radiation may be decomposed into a certain number of periodic disturbances, each of which is the simple element of every radiation. The usual manner of describing undulatory disturbances such as light, sound, heat, wireless telegraph waves, etc., is by the wave length, which depends on the number of vibrations made by the wave per second, and the velocity with which the wave travels. In order that we may better understand what these values are let us take a concrete example. In a vacuum, light travels 180,000 miles per second, or about three-quarters the distance from the earth to the moon. The wave-length of, for example, green light is about half a micron

(1 micron = 1/1000 of a millimeter = 1/25,000 of an inch) from which it would follow that the frequency would be the number of microns contained in 180,000 miles or 600,000,000,000,000 vibrations per second.

Lewis[1] has compared ordinary light to the sound produced by a drum which differs from the purer tone of a more highly developed musical instrument in that it emits a jumble of many such tones simultaneously, and such a jumble of tones we call a noise. By means of a prism it is possible to analyze white light into its component tones, and thus we obtain the spectrum, where at every point there is a definite spectral color corresponding to a perfectly definite frequency. The rays that the eye cannot perceive may be detected by the camera and other devices which have made it possible to extend the spectrum and to study radiant energy beyond the limits of visible frequency, and thus investigate the infra-red on the one side and the ultraviolet on the other. Indeed we now know that in all the phenomena of radiant energy, beginning with the low frequencies of wireless telegraphy through the infra red into the visible out into invisible ultraviolet, and from there on out to the region of X-rays, we are dealing with a single phenomenon, varying only in rate of vibration. Of all this vast keyboard of radiant energy less than one octave produces visual sensations.

In discussing the subject of ultraviolet radiation it is interesting to make a comparison with the length of other waves with which we are familiar, viz., the colors of the spectrum, heat waves, sound waves and electric waves.

The color spectrum ranges from .00065 mm. for red at one end of the visible spectrum to .00040 mm. for violet and .00012 mm. for extreme ultraviolet, which is the lower limit of the metallic arc. The lower limit of the mercury spectrum is .00022 mm. while the wave length most efficient for sterilization is .00028 mm.

Wave-lengths shorter than .00036 mm. are scarcely visible to the human eye. The upper limit of the infra-red rays as given off by a Welsbach lamp is .60 mm. The wave length of heat rays in about the middle of the infra red as measured by Rubens is .0107 mm., a shrill whistle sends out waves 13 mm. long, middle C on a piano has a wave-length of 1300 mm., short wireless telegraphic waves are in the neighborhood of 50,000 mm., while the ordinary 60 cycle alternating field current has a wave-length of 4990 million mm. or 3100 miles.

In order to illustrate these figures and put them in a form where we can get an idea of the comparative values of each, let us multiply them by the factor 10,000, which will give us in round numbers 1 mm. for extreme ultraviolet, or, say the thickness of an ordinary pin, violet would then be twice the width of the pin head, red would be a quarter the length of the pin, heat rays would have a length of 4½ inches, a shrill whistle would have a wave-length of nearly one and one-half city blocks, while middle C on the piano would give off waves eight miles long. The shortest wireless telegraph wave would then be 310 miles long, or the distance from New York City to Buffalo, while

[1] Chem. & Met. Engineering 1921, *24*, 871.

the 60 cycle a.c. field current would be 31 million miles or one-third the distance from the earth to the sun. The limiting values of ultraviolet wave-lengths and their place in the domain of elastic fluid undulations are thus strikingly illustrated.

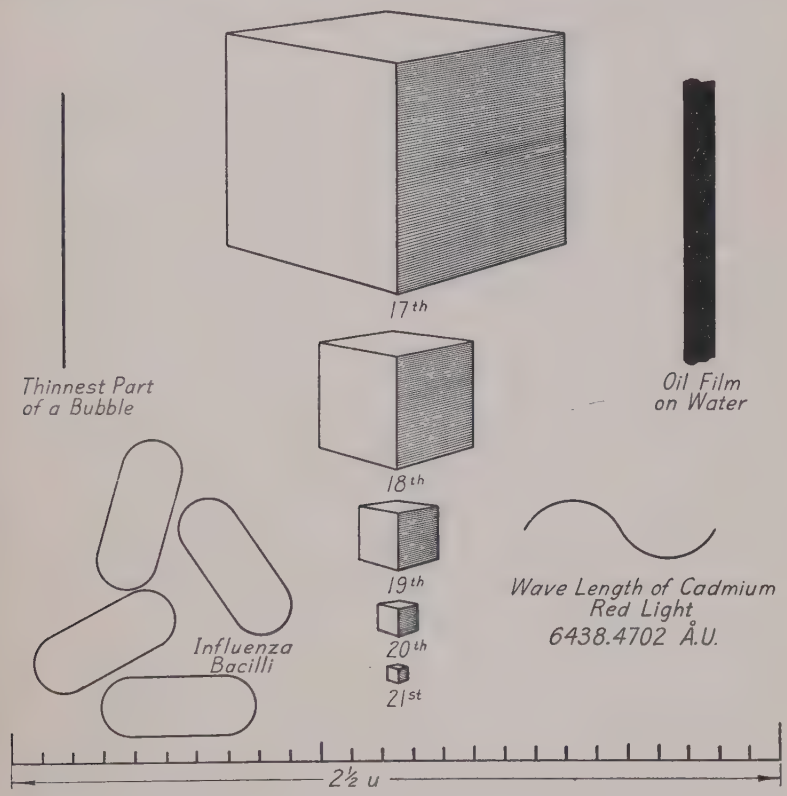
Spectroscopic measurement is reduced to wave-length or wave frequencies, by a process of interpolation between lines the wave-length of which are known with sufficient accuracy. A convenient unit is that adopted by the International Union of Solar Research and is called an Ångstrom (Å); and is equal to 10^{-8} cms. Perot and Fabry, employing their interferometer methods, have compared the wave-length of the red cadmium line with the standard meter in Paris and found it to be equal to 6438.4696 Å, the observations being taken in the dry air at 18° C. and at a pressure of 76 cms. (g. = 98.665). This number agrees singularly well with that determined in 1893 by Michelson who found for the same line 6438.4700. Perot's number is now definitely adopted to define the Ångstrom and need never be altered, for should at some future time further researches reveal a minute error, it will only be necessary to change slightly the temperature or pressure of the air in which the wave-length is measured.[2]

Aston [2a] graphically portrays relative magnitudes as shown in Figure 1. For convenience we will start with a standard decimeter cube of lead weighing 11.37 kilograms, which is progressively subdivided. The subdivision is carried out by three cuts at right angles to each other, dividing the original cube into eight similar bodies each having half the linear dimensions and one-eighth of its weight. Thus from the first division the cubes will have 5 cm. sides and will weigh 1.42 kilograms. On subdivision of these cubes in like manner the cubes obtained by the second cut will weigh 178 grams, by the fourth cut 2.78 grams and so on. It will be observed that diminution in the series is very rapid. As a result of the ninth cut a quantity of lead is obtained which is just weighable on the ordinary chemical balance. The results of further cuts receive comparison in the accompanying figure. The last operation possible without breaking up the lead atom, is the twenty-eighth.

Newton recognized the periodic constitution of light and measured the half wave-lengths, under the name of "intervals of fits." [3] These results obtained by Newton remained unused and even misunderstood up to the beginning of the nineteenth century, at which time Young and Fresnel found that the wave-lengths of luminous radiations form a continuous progression from the red to the violet. Fresnel doubled Newton's intervals of fits so as to give the wave-lengths. A long series of investigations, extending over nearly a century, contributed greatly to the existing means of separating and analyzing the radiations, such names as Fraünhöfer, Fizeau, Foucault, Kirchhoff, Bunsen, Ångström, Rowland, and Michelson standing out prominently. During this period the methods of measuring the various factors were brought to very great precision. All of this development of methods of measure-

[2] The Encyclopædia Britannica, Eleventh Edition.
[2a] J. Franklin Inst. 1922, *193*, 584.
[3] See Fabry, J. Frank. Inst. Sept. 1921.

ment, however, was made by means of visible radiations while at the same time progress was made in the discovery of other radiations which the eye does not perceive. The most commonly used device for measuring the longer radiations not perceptible to the eye is thermometric apparatus capable of absorbing radiation and transforming its energy into heat which can be measured very exactly. If however this radia-



Courtesy Franklin Institute.

FIG. 1.

tion is destroyed by absorption its energy is lost, therefore it became necessary to devise and discover means such that the absorption for the wave-lengths under consideration would be reduced to a minimum. The investigation of the spectrum from the thermal point of view seems to have been made for the first time by Herschell in 1800 who discovered that the solar spectrum was prolonged beyond the red. It remained however for other investigators, among them Ampère was perhaps the foremost, to identify the infra red completely. Methods were gradually perfected by the use of transparent materials other than

glass and by the invention of more and more sensitive thermometric apparatus. On the other side of the spectrum the invisible radiations might perhaps also have been studied by means of a thermometer, but on account of the weakness of these radiations in heating effect more sensitive detectors such as the photographic plate were used. First Daguerre plates, next wet collodion, followed by bromogelatine, and finally orthochromatic plates were employed.

If one passes progressively towards the short wave-lengths the study of the ultraviolet begins with a minimum of difficulty. The line of demarcation between the violet and ultraviolet radiations is not a frontier, either from a theoretical or technical point of view, as there is no difference in the nature of the two types of rays and the methods of study are identical in each case. As one advances however into the shorter wave-lengths the difficulties increase. At about wave-lengths 3400 Å glass becomes so strongly absorbing that it is no longer of service and must be replaced by quartz or some similar crystalline substance. At about 290 μμ (2900 Å) the solar spectrum ends due to the absorption by ozone in higher levels of the earth's atmosphere; but by artificial means, for example the metallic arc, the short wave-lengths may be supplied of satisfactory intensity. It is comparatively easy to photograph and measure wave-lengths as small as 185 μμ (1850 Å) this limit being reached by Cornu working from the year 1881 on. From this point the difficulties increase very greatly as quartz becomes strongly absorbing, the gelatine of the photographic plates becomes so opaque that the radiation does not penetrate it, hence no longer acts upon the silver salt and finally, air itself ceases to be transparent; all radiations being absorbed in a very small thickness. A little later Schumann overcame these difficulties by replacing the quartz with fluorite, photographic plates were made without gelatine and the apparatus was placed in a vacuum. Under these conditions the spectrum of hydrogen was obtained to 120 μμ (1200 Å) at which point fluorite ceases to be transparent. It may be noted, however, that in this investigation Schumann did not actually measure the wave-lengths but only estimated them using an extension of the dispersion formula for fluorite. In order to proceed further it became necessary to reject all the ordinary apparatus of optics, both lenses and prisms, and in their place reflect the radiations by metallic mirrors. This led to the use of the concave grating which has the advantage of giving directly the length of the waves. With the use of this instrument in vacuum Lyman succeeded in determining the lengths of the waves in the spectra studied by Schumann, and further in prolonging the spectra to 51 μμ (510 Å) in the spectrum of helium which is far beyond the transparency of fluorite. Millikan, using a concave grating in a very high vacuum and a high potential spark between metallic electrodes in the same vacuum, prolonged the spectrum to 13.66 μμ (136.6 Å) which is the limit so far reached in the study of radiations by optical means. This is not the limit of radiations of short wave-length, but great technical difficulties stand in the way of still further continuation.

While these radiations of the short wave-lengths were being investigated the discovery of Röntgen or X-rays revealed the existence of unsuspected radiations whose properties appeared to be at variance with optical radiations in that the new radiations moved in a straight line without apparent refraction or reflection and had the property of penetrating great thicknesses of nearly all bodies, even those which are opaque to all other radiations. From the early investigations of these radiations it was concluded that the X-rays were merely continuations of the gradually diminishing light waves having extremely short wave-lengths, that is to say, they were a hyper ultraviolet. This hypothesis explained the nearly complete absence of refraction and reflection if the wave-length was of the order of magnitude of molecular dimensions. To replace the grating formerly used, by the natural strata of a crystal was the next step. Laue conceived the idea that such a crystal should take the place of a grating having a ruling so fine that the distance between the rulings would compare with the distance between the particles within the crystal. On sending a bundle of X-rays through a crystal the expected phenomenon was realized. A short time later Bragg attacked the problem by studying the phenomena of reflection from a crystal which behaves like a medium made up of layers. From this point on, the problem of measuring the X-rays was easily handled. It being possible to determine the interval between the lattice planes of a crystal, all the elements were at hand required for the determination of the wave-length of the X-rays, measurements having been made to between 13.3 and 0.05 Å which are of the same order of magnitude as the dimensions of molecules.

Information on the zone of radiation represented by wave-lengths shorter than, say, 180 μμ (1800 Å) down to about 10 μμ (100 Å)—the realm of the X-ray—is so meager that this extensive region is practically unexplored. Unquestionably there exist in such an undulatory "No-man's land" forces of radiant energy capable of disuniting and reconstructing many chemical substances. Who, physicist or chemist, shall be the first to trample on the barriers which oppose our decisive entrance to this zone. What strange properties will matter be found to exhibit therein. Is it, perhaps, the key to the transmutation of some of the elements? Will gold, for example, be readily made from another metal, such as mercury; as Miethe now claims to have accomplished to the extent of obtaining traces of the more sought-for metal. Will the irradiation of—let us say—uranium, with these elusive rays (of selected wave-length) perhaps yield "synthetic radium" or radioactive substances. These and many other queries of an intriguing nature present themselves.

The generation of ultraviolet *in situ*, that is, actually within the solution, suspension or amalgam of the substance chosen for raying treatment is one possible manner of accomplishment. By allowing the extremely-short readily-absorbed waves, ranging from 100 Å to 2000 Å to act directly, without interposition of other media such as results when the source of ultraviolet is adjacent to a vessel containing the substance

under treatment, much of interest might be discovered in this fascinating experimental domain.

When the substances selected for irradiation are metals or other bodies unaffected by the heat of the arc these may be added to mercury or other appropriate arc-forming elements and thus rayed *in situ*. Organic bodies, of course, cannot be irradiated in this manner. A method of direct radiation or generation of ultraviolet *in situ* at relatively low temperatures remains to be developed. Perhaps substances fluorescing in X-rays to emit radiation of the wave-length of "No-man's land" can be discovered. The operation then would be comparatively simple: dissolve or suspend the substance in a solution of the fluorescent body and expose to the X-rays.

Of far greater consequence would be the discovery of substances having the equivalent effect of "reverse" fluorescence, that is, capable of changing the longer wave-lengths to shorter ones. From sunlight, then, we would have the means of causing ultraviolet effects *in situ*.

In order to conduct research in the field of synthetic foodstuffs it should not be necessary first to learn the tricks of chlorophyll in creating vegetation: whether or not it steps sunlight up to ultraviolet or down to infra red. The complexity of the reactions involving chlorophyll makes an explanation of its mechanism a large issue.

The experimenter who patiently searches for substances capable of transforming wave-length—be these fluorescent in the ordinary sense or possessing the equivalent of "reverse" fluorescence—may be able to aid in large measure in the solution of some of our major problems.

Perhaps the arid but sun-bathed lands of Arizona and New Mexico at some future day can be made to blossom in a chemical sense through the agency of light-wave transformers.[3a]

There is also interesting speculation for the physicist in the possible properties of rays in the transition stage from X-rays to definite ultraviolet radiation. Starting from the side of the X-ray and going towards the increasing wave-lengths one should find radiations more and more easily absorbed; this absorption should then pass through a maximum and gradually decrease. At a certain point the reflective power of metals should begin to be evident. A refraction which is zero for the X-rays and very marked for the ultraviolet rays should begin to appear but its

[3a] Mathews very forcefully remarks, Ind. Eng. Chem., 1923, 887, that another photochemical problem of great interest, and one which has excited the imagination of the scientists of many generations, is the possible utilization of the enormous quantities of radiant energy coming from the sun. Waste places, now useless for any purpose, may eventually become the sites of great manufacturing plants, once the secret of transforming radiant energy into chemical energy is solved. Here we have an unlimited and almost constant source of energy of enormous magnitude, and one which by its successful utilization will tend to neutralize in a large measure the effect of our diminishing coal and oil supply. While the coal and oil problem may not be a serious one for the present generation, surely the time will come when other sources of energy supply must be found and utilized if civilization is not to perish. Knowing that hundreds of billions of horse power of radiant energy are constantly coming to the earth from the sun, it is not strange that the photochemist casts a speculative eye toward the possible utilization of this enormous amount of energy, a very considerable portion of which is now entirely wasted.

beginning would probably be very difficult to determine on account of the absorption and it is predicted that this region will be the most difficult of all to explore. Holweck [3b] has made some progress in this field using an apparatus which consists of a sort of Coolidge tube made entirely of metal on which the cathode and anode are separated by the distance of one millimeter, being worked under an exceedingly low potential (between 25 and 1800 volts). To detect the rays, their ionizing properties are utilized. As the rays emerge from the tube they enter an ionization chamber containing air at a pressure of one millimeter, existence of the radiation being manifested by the electric conductivity of this air as measured by an electrometer.

While from the above it may appear that the investigation of some of these rays is fairly complete, we have only to note the still vast unexplored regions of the properties of each of these wave-lengths which have so far only been measured, to realize that the investigations heretofore conducted are merely preliminary trips and that the real investigations are yet to be made. The difficulties which evidently surround the worker in this field appear to be almost insurmountable at present, due to scarcity of really fine natural crystals of quartz, calcite, and fluorspar, without which it is almost impossible to investigate the regions of short wave-length. Another difficulty arising is the ruling of gratings which must be ruled at times with more than 100,000 lines, all at exactly equal intervals, and up to the present the production of such gratings is exclusively an American industry, no European instrument maker having ever produced a single grating of any value as an instrument of research.[3c] At present the demand for such gratings greatly exceeds the supply. Finally there is a great need of perfecting the apparatus for detecting radiation. The photographic plate is especially well adapted for this purpose, but the range of its sensitiveness is limited. The thermometer, although in recent years greatly improved, is still very far from being satisfactory as to sensitiveness. The photoelectric cell and similar electrical detectors can render great service for measurements of intensity but they are lacking in power of definition and their sensitiveness is strongly selective. We see then that if the rôle of the explorer is reaching its end in the domain of luminous radiations there still appears a considerable task for the technician to accomplish.

In the aggregate the existent knowledge on the chemical action of ultraviolet constitutes a very considerable mass of facts. These however are scattered over so wide a field that their coordination and correlation is by no means a simple task. The difficulty is much increased due to the lack in many investigations, especially the earlier ones, of adequate data on the approximate wave-lengths employed. Such information is important since, on many substances waves of different length produce dissimilar, and in some cases, totally opposite effects. With the growth of photochemistry, this condition will be gradually overcome, data will

[3b] Some spectroscopic measurements have been made by Holweck in the region between 140 and 12A, Compt. rend. 1925, *180*, 658.

[3c] Note Fabry, J. Frank. Inst. 1921, *192*, 277.

be supplied to fill in the gaps and the laws governing radiation will be better comprehended. At the present time much interest is displayed in what may be termed the photo-equivalence law of Einstein and the radiation hypothesis of Lewis-Perrin (discussed in Chapter 5). Photochemists are now striving not so much for the accumulation of facts on the synthesis and photolysis of chemical bodies as they are to establish the laws which govern the union and disunion of the elements and their compounds under the action of radiation. The establishment of laws governing such changes would make it possible to predict in a large number of cases the outcome of radiation of a given character. There is no question therefore of the importance of investigations tending to confirm the Einstein and Lewis-Perrin proposals or to replace these by others which may better fit the facts. Aside from the foregoing it should be noted that the principal fields of study and investigation which are now occupying the attention of photochemists are the synthesis of carbohydrate and protein material by the aid of light or ultraviolet radiation (discussed in Chapter 11), the improvement of monochromatic light sources and the production of cold light. This last mentioned subject is of great practical interest as our modern methods of producing light by heating bodies to incandescence is decidedly wasteful. The production of light without heat and therefore the elimination of the loss of energy due to radiated heat would of course represent a revolutionary step. Considerable progress has been made by Harvey and others in the field of luminescence and phosphorescence through a study of living creatures capable of emanating cold light, such for example as the firefly or glow-worm. These subjects, however, take us beyond the scope of the present volume. The other topic of investigation mentioned above, namely the improvement of monochromatic light sources, is beginning to receive a considerable measure of attention and many developments in this direction during immediate coming years are predicted. With better means for research such as is likely to be afforded through refinements in apparatus giving radiation of definite and limited wave-length the possibilities of photosynthesis and photolysis will be greatly expanded.[4]

[4] According to Kowalski-Wierusz, U. S. Patent 1,207,347; J. S. C. I. 1917, *36*, 90, distinction must be made between three different zones of ultraviolet rays, corresponding to the effects which the rays produce. The first zone, or the initial ultraviolet extends from the visible spectrum to about a wave-length of 3000 Å. The radiation which corresponds to the rays of this zone is abundantly emitted by the sun. It is but slightly absorbed by the atmosphere. The photochemical reactions which this radiation produces are exothermic almost without exception. The physiological and biological properties are similar to those of the adjacent blue and violet radiation, but more intense. This radiation exerts almost no destructive action on the lower forms of life, such as bacteria. The second zone comprises the so-called middle ultraviolet; and extends from about 300 to 200 μμ (3000 to 2000 Å). Only the first part of this zone is found in sunlight. The rays of this zone are strongly absorbed by many substances, and therefore the photochemical effects of this radiation are very intense. Finally, the third zone, the extreme ultraviolet, corresponds to wave-lengths of about 200 to 100 μμ (2000 to 1000 Å). This zone can hardly be technically considered at the present time, because radiation of this kind is completely absorbed by a few centimeters of air. The middle ultraviolet rays may be produced by means of a spark gap,

One method of ascertaining the effectiveness of various wave-lengths, which has found frequent use, is the procedure of applying to a glass plate a coating of the substance to be rayed and exposing this to the spectrum of a quartz spectrograph. Such a method has been used in bactericidal determinations. Thus, Browning and Russ [5] coated a glass plate with a thin layer of nutrient agar, painting it with microorganisms and exposing to the spectrum. After exposure and incubation, that part of the plate extending from 2490 to 2380 Å was found covered with clear lines corresponding to the emission lines which had produced the bactericidal effect. Mashimo [6] has obtained excellent photographs on incubated plates in this manner. Likewise Pfund used the method advantageously to determine the effect on lithopone of different wave-lengths [7] of the ultraviolet spectrum. (See page 140.)

Finally, we may remark that the theory of light holds aloof, as it were, from approach to a settled status. By assuming light to be a transverse wave motion spreading out from its source various phenomena such as interference are readily explained. On the other hand, a considerable number of effects are better elucidated on the basis of the quantum theory, according to which quanta or "bundles of energy" are emitted from the source at intervals. (See Chapter 5.) Thus the quantum school is able adequately to apply its teachings over a considerable field, notably to photoelectric phenomena, Bohr's theory of the atom and the relationship between the wave-lengths of lines in emission spectra. The rift between these two conceptions is a wide one and the separation is so complete that each school finds little in common with the other. In present form neither the wave nor the quantum hypothesis appears to provide the means for explaining the phenomena of light in various aspects. Each school justifies its existence by the interpretation of particular phenomena which the other cannot explain. In fact, each hypothesis seems in many cases to exclude the occurrence of phenomena which have actually been observed. Obviously, this is an unsatisfactory condition which demands and is receiving extensive investigation by a group of scentists, including Bohr, Lorentz and others well qualified to advance toward a theory of light of a more fitting character.[8]

and these radiations between 290 and 210 μμ (2900 and 2100 Å) are effective for sterilization purposes. The investigations of Henri have indicated that the shorter the wave-length, the more intense is the bactericidal action of the radiations. Other investigations have shown that the calcium ion strongly absorbs the short wave-lengths.

[5] Arch. Radiol. and Electrotherapy, 1918, *18*, 85.

[6] Mem. College of Sci., Kyoto Imperial Univ. 1919, *4*, 1.

[7] In the text which follows, units of wave-length are commonly designated in terms of μμ, with the equivalent wave-length in Ängstrom units frequently set alongside for comparison. In converting from one unit to another it should be borne in mind that the micron, or μ, is 1/1000 of a millimeter and that the unit μμ is 1/1000 μ, or 1/1,000,000 of a millimeter. The Ängstrom unit, numerically, is ten times greater than μμ and is therefore 1/10,000,000 of a millimeter, or 1 Å $= 10^{-4}$ micron $= 10^{-8}$ centimeter $= 10^{-10}$ meter. This unit, selected at a time when we had scant knowledge of molecular dimensions, happens to be of about the same order of magnitude and is suited for studies of atoms and X-rays.

[8] Note Stoner, Proc. Cambridge Phil. Soc. *22*, Pt. 4.

Chapter 2.

Sources of Ultraviolet Rays.

The amateur who for the first time undertakes to dabble with ultraviolet rays and the experimentalist who makes his initial investigations with these invisible radiations usually are surprised to find the principal source of these rays is from metals in a state of vivid incandescence. To be sure, there is the so-called chemical lamp such as that of Wulf, burning carbon disulfide in oxygen, but such means are troublesome to operate and generally possess a very limited range of radiation. That great body of incandescence, the sun, popularly supposed to provide us with beneficent ultraviolet rays, does in fact emit ultraviolet radiation in superabundance into interplanetary spaces but when these rays impinge on the outer layers of the earth's atmosphere, transparent though the latter be to the eye, absorption is so great that only a minute proportion of these rays penetrate to the habitations of mankind.

Since the vivid incandescence of metals readily furnishes ultraviolet radiation how should we best obtain a temperature adequate for the purpose. The employment of electric current immediately comes to mind. By means of a high tension disruptive spark or by establishing an arc between metallic electrodes ultraviolet radiation is conveniently produced. For the amateur who wishes to impress his friends with the magic of ultraviolet by displaying numerous fluorescent effects—those striking transformations or step-downs—of the invisible rays into visible light, the high tension spark between iron electrodes is the simplest device. Let us not create the impression however that the spark method is only for the tyro. This method of generating ultraviolet radiation applied in vacuo has been responsible for revelations of great importance in the domain of the ultraviolet of very short wavelength.

Apart from the very restricted ultraviolet radiations present in variable quantity from day to day in sunlight; all depending on the amount of moisture present in the air and other atmospheric conditions, the principal sources of ultraviolet rays are:

1. Lamps burning certain fluids in oxygen, the so-called chemical lamps or other devices of a similar character. These are of very restricted application.

2. High tension disruptive electric spark discharge between metal electrodes, for example iron, nickel, cobalt, copper, tungsten, zinc, magnesium, aluminum and cadmium. These form the basis of simple apparatus useful in producing fluorescent effects.

3. Establishment of an arc between electrodes of solid metal such as iron or iron and carbon, usually without exhaustion of the air.
4. Mercury vapor arcs, especially those created in vacuo.

As noted in Chapter 1 ultraviolet radiation is a potent agency in the disruption of chemical substances. Since it is absorbed by those substances which it destroys, its very potency makes its transmission difficult. Air and other gases, water vapor and in fact most substances absorb it so effectively that after traversing any of these media for a short distance penetration ceases. There are available for ultraviolet investigations such as enclosures for arcs, filter cells and exposure vessels only a very few materials. Among these the outstanding material is transparent quartz. The fusion and working of quartz to make transparent articles is a comparatively recent development and expansion of the utilization of ultraviolet radiation has fairly well followed the advance in technique in the working of quartz. Only a short time prior to the publication of this volume an announcement was made by Berry on the production of fused quartz in large quantities by means of special electric furnaces of the vacuum type which enable clear quartz articles of large dimensions to be made comparatively cheaply. Quartz however does not transmit ultraviolet rays of a wave-length shorter than about 1850 Å and in the field of shorter wave-length other substances transparent to ultraviolet rays must be used. With the shortening of the wave-length the number of materials capable of transmitting such radiation is reduced to so small a number that we practically have only calcite and fluorite available. It is a matter of interest in passing to note that the visible rays of the solar spectrum penetrate glass and many other substances giving the property which we describe as transparency or translucency, while the ultraviolet rays except for the longest ones adjacent to the blue end of the spectrum of visible light cannot penetrate glass nor do they travel far in most of the materials which we commonly regard as transparent or translucent. Yet on passing down through the long range of the ultraviolet spectrum we finally reach the region of the X-ray, the extraordinarily penetrative qualities of which, to materials which we ordinarily denominate as opaque, have brought so many marvelous aids to medicine and chemical research.

Let us hope that some of the investigators of the future instead of devoting the major part of their effort in ultraviolet radiation to the study of the effects of the rays on different substances will search far and wide for materials transparent to ultraviolet radiation especially of very short wave-length. Much could be accomplished in the chemical world through apparatus adapted to generate these potent rays. The field of mineral substances already has been well canvassed but we may point out that there may be some opportuntiy in the direction of synthetic solids such, for example, as the glass-like substances obtained by reacting on urea with formaldehyde.[1]

[1] See Ellis, Synthetic Resins and Their Plastics, New York, 1923, Chapter 13, Urea and Thiourea Resins; also Pollak, Chemical Age, New York, Oct. 21, 1924; Chem. Ztg. 1924, *48*, 97.

Returning to the topic of this chapter, mention has been made of the chemical lamp devised by Wulf.[2] He investigated various sources of ultraviolet rays and discarded the Nernst lamp because it yielded too little ultraviolet radiation and the carbon arc because of its fluctuating quality. Wulf then constructed a lamp as shown in Fig. 2. Carbon disulfide and oxygen are supplied through brass tubes to the mouth of a burner, above which is suspended a small copper ball to bring about the rapid admixture of the carbon disulfide vapors and oxygen. An intense white light is produced by a flame 20 to 30 centimeters in height. A metal chimney placed slightly above the base of the flame

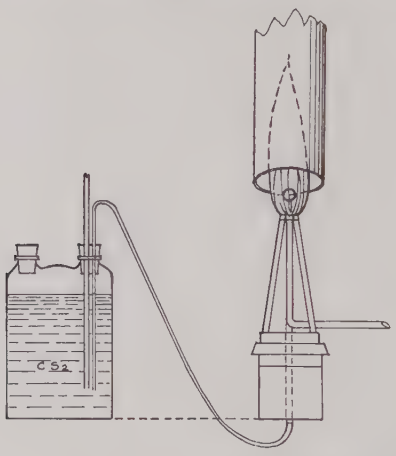


FIG. 2.—Wulf's Carbon Disulfide Burner.

cuts off the upper fluctuating portion of the latter and thus yields a very constant source of light.[3]

The high tension disruptive electric spark between iron terminals is very rich in ultraviolet radiation useful to produce fluorescent effects. Other metals such as zinc, magnesium, nickel and cobalt product a radiation more intense than iron in certain regions of the ultraviolet spectrum but iron shows a more uniform distribution throughout the range generally desired for fluorescent effects. Iron electrodes therefore have been adopted in a spark outfit designed by Andrews.[4] The connections of the apparatus are shown in Figure 3. A small transformer steps up a 60-cycle 110-120 volt alternating current to about 4000 volts. A condenser is connected in series with

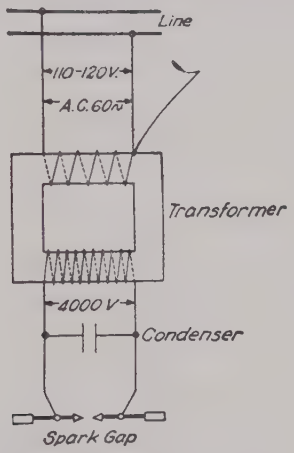
[2] Ann. Physik. 1902 (iv), 9, 946. Tassilly and Gambier, Compt. rend. 1910, *151*, 342, burned carbon disulfide in nitric oxide.

[3] Care should be taken that the carbon disulfide and oxygen do not mix until the desired point of combustion is reached. As is well known carbon disulfide is a very inflammable and explosive substance and the production of ultraviolet rays in this manner is not without danger.

[4] Gen. Elec. Review, April, 1916, 319.

the iron terminals. The spark gap is adjustable. Assembled apparatus is shown in Figures 4 and 5. As this apparatus uses only about 250 to 300 watts it can be safely connected to any alternating current lighting circuit.

On the other hand the employment of aluminum terminals is recommended by Ross.[5] Terminals used by him were 3 mm. x 8 mm. in cross section and were placed 7 centimeters apart on iron plates. Small dishes containing ice resting on the metal served to conduct away the heat rapidly. The terminals were connected in the secondary circuit of a large induction coil used as a transformer. In the secondary circuit a large Leyden jar was joined in parallel. Through the primary circuit there was passed an alternating current of 110 volts and 3.4



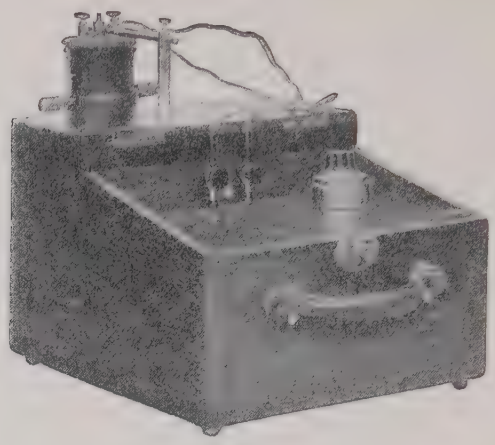
Courtesy General Electric Co.

FIG. 3.—Diagram Showing Connections, "Iron Spark" Apparatus.

amperes. With terminals of aluminum Ross found the intensity of the ultraviolet radiation measured by the decomposition of potassium iodide to be twice as great as that resulting when terminals of any other common metals were used. After every observation the aluminum terminals were sharpened and then placed the same distance apart so that each exposure could be begun under the same conditions. Cadmium is not recommended because of its softness.

The difficulty with such devices as those of Andrews and Ross employing a spark is the maintenance of constant conditions. When observations are to be conducted over a considerable period during which the intensity of radiation must not alter, the high tension disruptive

[5] J. Am. Chem. Soc. 1906, 786. Grebe, Zeitschr. wiss. Photographie 1905, *3*, 376, also used aluminum electrodes which however were submerged under flowing water. The electrodes were found to give off a considerable amount of oxygen and to wear away quite rapidly so that continuous adjustment was required. A zinc arc submerged in various liquid substances has been used for reducing effects by Stock, Brandt and Fischer, Ber. 1925, *58*, 643.

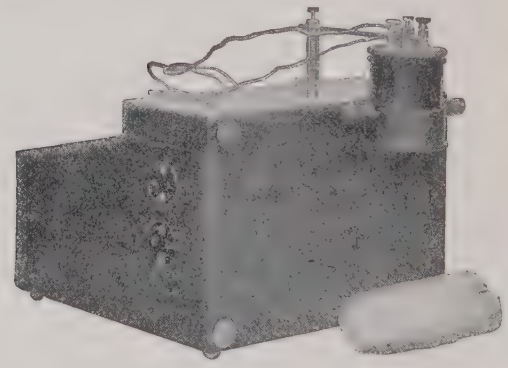


Courtesy General Electric Co.

FIG. 4.—Rear View of "Iron Spark" Apparatus.

spark between metallic terminals ordinarily cannot be advantageously employed.

Thus for some purposes the spark between metallic electrodes is satisfactory but in general the quantity of ultraviolet energy is far less than that available through the use of arcs. The short spark obtained



Courtesy General Electric Co.

FIG. 5.—Front View, Portable "Iron Spark" Apparatus.

from a transformer may be satisfactory or it may be necessary to "fatten" by using a condenser. A high-frequency spark occasionally is required.

High-frequency oscillations set up by means of a Tesla coil have been used by Howe [5a] to produce a spark between aluminum electrodes

[5a] Phys. Rev. 1916, *8*, 674.

placed under distilled water. Howe has reported that this source gives a continuous spectrum which on long exposures extends to 2100 Å. Strachan [5b] likewise used high-frequency oscillations with a Tesla coil but employed brass electrodes under water. Using from four to six kilowatts in the primary of the transformer, he secured a very satisfactory continuous spectrum extending to 2200 Å. Fulweiler and Barnes [5c]

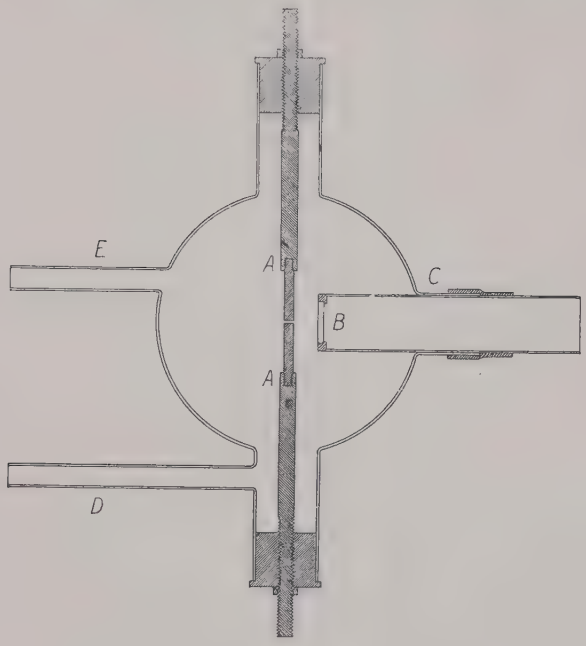


FIG. 6.

attempted to pattern an apparatus after Howe in order to obtain a continuous ultraviolet spectrum. After making a number of modifications, the principal one being the omission of the Tesla coil, an arrangement was obtained (See Figure 6) which afforded good results.

The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These were mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the side tubes of a pyrex glass bulb of about 500 c.c. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. Fulweiler and Barnes found under the electrical conditions used that a spark length of about ½ mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E. For the production of the spark Fulweiler

[5b] J. Franklin Inst. 1922, *194*, 84.
[5c] *Ibid.*, 83.

and Barnes employed at G. E. X-ray transformer, type K, using 15 amperes from the 110 volt A.C. mains on the primary coil. A mercury interrupter which made and broke a D.C. current about 120 times a second was also employed. For capacity, two Leyden jars of about .001 m.f.d. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Figure 7 shows this electrical circuit where T is the transformer; C, the capacity; S, the external spark gap and W, the tungsten spark. The choice of

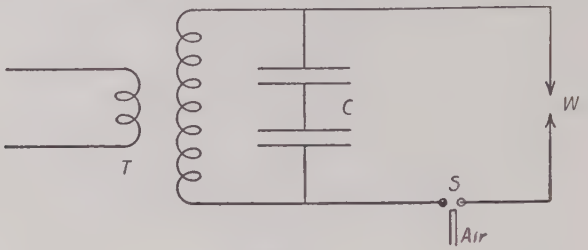


FIG. 7.

tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon and molybdenum. The tungsten gave more rays in the shorter wave-lengths and required very much less adjustment. Using 1.6 kilowatt in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. Figure 8 illustrates the continuity of the spectrum thus obtained. The absorption bands are those of a 0.1 per cent solution of benzene in ethyl alcohol.

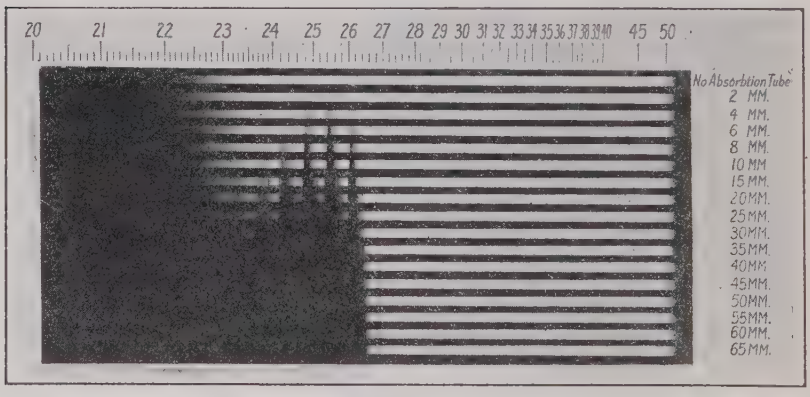


FIG. 8.

The lengths of the solution used are indicated on the side of the plate. This photograph was taken with a Hilger quartz spectrograph. The top exposure with no absorption tube indicates the uniformity of the irradiation. In the original negative the spectrum extends to 2050 Å.

Kowalski [6] found the oscillating spark using invar electrodes to be an economical source of ultraviolet rays. To increase the amplitude, the capacity of the oscillating circuit must be as great and the induc-

[6] Elec. Rev. West. Elec. 1915, *66*, 1055.

tions as small as possible. Kowalski [7] also shows that the region of maximum radiated energy is displaced towards the longer wave-lengths as the oscillatory current is increased. Increasing the amount of energy consumed in the spark, however, causes displacement toward the shorter wave-lengths, but this displacement is dependent in a degree upon the nature of the electrodes. The intensity of the mean ultraviolet ray, used in photochemical reactions and in sterilization, varies inversely with the frequency. A definite relation can be established between the number of sparks per second, capacity, and frequency of the primary current, if a resonance transformer is used.

A radiation of short wave-length described by Reboul [8] was subsequently studied by Reboul and Bodin.[9] This radiation is of a wave-length between that of the ultraviolet and X-rays, and is capable of ionizing gases, and affecting a photographic plate or electrometer. The rays are produced when cells composed of pastilles of metallic compounds, previously powdered, are traversed by an electric current. The radiation is thought to be due to the variation in speed of the electrons in traversing a sharp potential gradient. It depends on the chemical composition and state of aggregation of the material employed and, for a given compound, the intensity of the radiation depends on the potential employed; small increases in the potential sometimes causing enormous changes in the intensity of the radiation. For a given substance, the intensity of the radiation is also increased when the current is increased, but, in general, cells with the smallest resistance and therefore carrying the largest currents emit least radiation. The coefficients of absorption of the rays by air vary from 9 to 15 centimeters and diminish as the distance of the grid electrode from the cell is increased. The radiation is therefore probably complex and can be separated by passage through gaseous layers of varying thicknesses.

We now arrive at the consideration of the production of ultraviolet radiation by the arc method. As previously noted arcs may be produced between solid electrodes exposed to the air or in an atmosphere of a metallic vapor such as mercury in an enclosing vessel of quartz. An arc produced between iron electrodes is a common expedient. More elaborate devices employ electrodes containing mixtures of metals. For example one type employs a positive pole of copper and a negative pole consisting of a sheet steel tube packed with a fine powder consisting principally of oxides of iron (magnetite), titanium and chromium. The enclosed or flame arc has been advocated as a source of ultraviolet rays of the longer wave-lengths. The mercury vapor arc has the advantages of steadiness but has large gaps in the spectrum and the ultraviolet energy decreases in the case of old lamps. Some old quartz mercury arc lamps have been found only half as effective as when first used. The ordinary carbon arc emits a considerable

[7] Compt. rend. *158*, 1337; Bull. Soc. Int. Elec. 4, 437.
[8] Compt. rend. 1920, *171*, 1502; *172*, 210; 1921, *173*, 1162; 1922, *174*, 1452.
[9] Compt. rend. 1924, *179*, 37.

quantity of ultraviolet rays in the near and middle regions of the ultraviolet. An arc which would emit a practically continuous spectrum between 200 and 400 μμ (2000 and 4000 Å) would be desirable. While the quartz mercury arc emits many lines in this region, the spectrum by no means approximates continuity. The ultraviolet spectrum of a tungsten arc is rich in lines in this region and such an arc can be made to operate quite steadily in certain gases. Argon has been recommended for the purpose.

An arc which will emit ultraviolet energy strongly may be simply constructed, employing an iron rod and a carbon rod for the two poles. Or two iron rods may be used. These poles are cooled by means of heavy brass or copper sleeves which may be moved along the iron rods as the latter are consumed. Thus the upper pole (negative) may be an iron rod about one-quarter inch in diameter. This is surrounded by a movable but well-fitted solid sleeve of copper about one inch in diameter. The lower pole may be an iron rod about one-half inch in diameter with hollowed end. One pole should be adjustable vertically. In preparing the arc a bead of molten metal is developed in the dished end of the lower electrode. The upper electrode is well cooled and the arc is maintained very steadily between the bead of molten iron and the upper solid electrode. Luckiesch has had such an arc operate at a rather high current density for thirty minutes without any adjustment.[10]

Nagaoka and Suguira [11] describe an arc having as a cathode a carbon rod coated with barium or strontium oxide, sheathed in a silica tube. Various metals or salts in a similar silica tube serve as the anode. The arc operates in a vacuum, and at 1500 volts produces rays which penetrate aluminum foil. Vaporization of the metal, short life of the arc, and the necessity of cooling and pumping are among the disadvantages.

The flame arc has received consideration as a source of ultraviolet rays, owing to the diversity of materials with which the carbons may be impregnated. The experiments of Mott and Bedford [12] with the light of the snow-white flame arc show extremely little ultraviolet in the spectrum region beyond 3000 Å. The ultraviolet rays of the snow-white flame arc give no ozone odor, which is so very marked with the quartz mercury arc. Also there is far less coagulation of egg-albumen than with the light of the yellow flame bare arc. Spectrum plates taken with a concave grating spectroscope show a marked decrease in photographic effect in the region of about 3000 Å compared with other flame carbons or the open carbon arc. Although special flame carbons have been designed to give ultraviolet rays in the region from 3000 Å to 2000 Å where the quartz mercury arc has some of its most powerful

[10] For a discussion of the relative merits of the mercury vapor lamp and the iron arc as sources of ultraviolet rays in determining the behavior of lithopones in water, glycerol, oils and varnishes see Gardner and Holdt, Paint Manufacturers' Assoc. Circ. 194, 1923.

[11] Astrophys. J. 1923, *57*, 86; Chem. Abs. 1923, *17*, 1753.

[12] J. Ind. Eng. Chem. 1916, 1029.

lines, the white flame arc is designed to have a spectrum extending into ultraviolet like sunlight.

An enclosed tungsten arc lamp[13] is described by Morphy and Mullard.[14] In the operation of this lamp a tungsten filament which also forms the electrode, is heated by a shunt circuit, closed temporarily when the lamp is switched on. The ionization of the gas brought about by the hot filament permits a current to pass across the gap to the tungsten globule which forms the other electrode, thus striking the arc, which can then be maintained indefinitely. When the lamp is run with a sufficiently high current the output of ultraviolet radiation is of the same order as from the open tungsten arc and the objections of unsteady working and the production of white fumes of tungsten oxide are avoided.

Schönn[15] describes apparatus and methods of observation of short wave-lengths especially in the region of the ultraviolet. Kinraide[16] furnishes details of an inexpensive lamp for the continuous production of ultraviolet rays involving the use of an electrode spreading out in fan shape to serve as a conductor of heat. This arrangement improves the efficiency due to the cooling effect. The Zeiss optical works have produced an arc lamp in which the carbons are impregnated with salts of iron which are found to give a light rich in ultraviolet rays. Screens are placed around the arc which cut off most of the luminous rays and those of greater wave length.[17] According to Gehloff[18] gas-filled tungsten or tantalum lamps, having a quartz window, furnish ultraviolet rays down to 2200 Å. Macdonald[19] produces ultraviolet rays by means of an arc operating in a vacuum having electrodes of gold alloyed with copper or silver. For other observations on the construction and properties of metallic arc lamps see Kowalski-Wirusz,[20] Luckiesh,[21] and Bell.[22]

[13] Designated the Quartz Pointolite Lamp.
[14] J. Roentgen. Soc. 1916, *12*, 70; Chem. Abs. 1917, 235.
[15] Ann. der physik. 1880, *90*, 483.
[16] Electrical Review, 1906, *48*, 775.
[17] Electrical Review and Western Electrician, 1913, 62, 813.
[18] Z. tech. physik. 1920, *1*, 224.
[19] British Pat. 206,588, Aug. 9, 1922.
[20] French Pat. 468,215, Feb. 15, 1914.
[21] J. Frank. Inst. 1918, 552.
[22] Elec. World, April 13, 1912.

Chapter 3.

Metal Vapor Lamps. Mercury Arc Lamps.

Since the use of the mercury arc came to be recognized as a reliable source of light of short wave-lengths the number of types of lamps embodying its use has increased rapidly. Some of these lamps appear to be make-shifts where lamps of standard design could not be obtained while others are attempts of one kind or another to improve the commercial types. While in this country there are recognized three principal types of quartz mercury lamps, many other types and modifications are included to show the trend of development of the field.

The fact that a brilliant light is emitted when mercury is vaporized in an electric arc Perkins [1] considers to have been originally observed by Wheatstone in 1835, who described its characteristics before the British Association. Its illuminating power was, however, not realized until some time later, when in 1852 Jackson took out a patent for a mercury lamp. It consisted of carbon electrodes, the lower one of which had a recess to contain a small quantity of mercury, the idea being to provide a non-consuming electrode. Binks about a year later produced and patented a lamp having two mercury electrodes which were enclosed in a glass case. Provision was also made for condensing the vaporized metal to the liquid condition again. Way patented a lamp in 1856 which was described in the London *Times* of August 3, 1860. It was stated that this lamp produced a more brilliant light than had ever been seen before. A jet of mercury was caused to fall into a fireclay cup. In another form two streams of mercury connected with the opposite poles of a battery played against each other from pipeclay jets. The details are as follows: Mercury is caused to fall from a jet in a thin stream, into a cup; the jet being about one-half inch above the cup. The upper reservoir and lower vessel are in connection with the poles of a Bunsen battery. As the current passes through the stream of mercury it scatters and diffuses it, producing a most intense light. The mercury vapor is confined by a glass cylinder which is made of sufficiently small diameter so that the heat of the arc will prevent the condensation of globules of mercury on the glass walls.[2] Harrison, in 1857, produced a lamp in which a carbon rod was suspended over a cup of mercury. He also devised a method of using multiple electrodes. In another form of lamp, mercury was caused to drop on a carbon rod, but owing to the difficulties

[1] Trans. Far. Soc. 1911, *6*, 199.
[2] Phil. Mag. 1860, IV, *20*, 249.

of obtaining a steady arc he endeavored to control it by means of an electro-mechanical device. In 1867 Siemens made a mercury lamp which had a vibrating electrode dipping into a mercury cup. The light of this lamp was, however, of an intermittent nature. Siemens' idea was to employ this lamp for lighting buoys at sea, but apparently the device never was employed for this purpose. The next attempt to produce a mercury lamp appears to have been made in 1875 by Prosser. It was a combined carbon and mercury lamp, the object being to overcome the flickering which was an unpleasant feature of the original arc lamps. Among the various other attempts to produce a satisfactory lamp must be mentioned that of Rapieff in 1879. This lamp contained a condensing chamber for the mercury vapor, and could be started by shaking the mercury or by an electro-mechanical arrangement. Very little advance seems to have been made until 1896, when Dowsing and Keating made the first true vapor lamp. They employed the principle of the Geissler tube—that is to say, a partially evacuated tube—and employed an alternating current, but found it advisable to warm the mercury before starting the lamp in order to vaporize it.

The first lamp which attracted any public attention was that invented by Cooper-Hewitt. The original lamp, the result of long experimenting, was produced in 1901. One of the difficulties with the mercury lamp was the tendency for it to become extinguished, owing to the raising of the electrical resistance as the pressure of the mercury vapor increased. By a determination of the vapor resistance Cooper-Hewitt was able to devise a lamp in which the mercury was cooled and condensed at about the same speed as it vaporized.[3] In 1902 Arons showed that a lamp could be produced by passing a direct current through mercury vapor in an evacuated tube. According to Axmann [4] the later types of mercury vapor lamps are based on Arons' investigations.

For the purpose of making investigations in the extreme ultraviolet Wolff [5] used a quartz lamp of the Stark and Kuch type [6] made by Heraeus (Figure 9). The lamp A has a water-cooled side tube B which is connected with a Geissler tube shown on the right. The latter is closed by a perforated plate K, over which is fastened a fluorite plate F. The tube H of the lamp A is connected to a pump. In order to control the time of exposure and to avoid the presence of metal vapors in the Geissler tube and on the fluorite window, a valve of sheet iron G is arranged in the tube B in such a manner as to be actuated by an electromagnet placed outside the tube.

[3] The original lamps were made with glass, which absorbs a very large portion of the ultraviolet rays given out by the mercury vapor arc, and were therefore of slight value as a source of these rays. On the introduction of clear fused quartz into commerce, mercury vapor lamps of transparent quartz were made.

[4] Zeitsch. Phys. u. diatetische Ther. 1909-10, *13*, 470.

[5] Ann. Physik. 1913 (IV), *42*, 825.

[6] Phys. Zeitsch. 1905, *6*, 438.

A modified form of lamp used by Wolff is shown in Figure 10. An elongated glass bulb set in a water bath, has two tubes in the lower side for mercury. An exhaust tube is situated at the top, and at the right hand end is placed a fluorite window. The mercury vapor con-

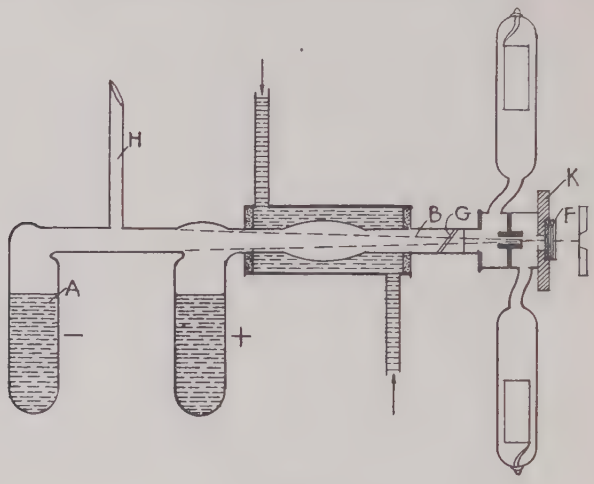


FIG. 9.

denses on the walls of the bulb so effectively that the window does not become coated with mercury even after operating for a considerable period. This lamp is started by an induction coil and operated at 220 volts. Fischer[7] constructed a mercury arc lamp suitable for chemical purposes which he used in experiments on the formation of

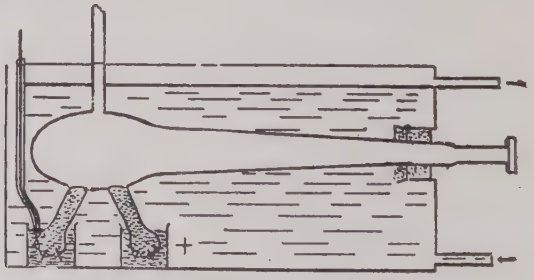


FIG. 10.—Modified Form of Lamp Used by Wolff.

ozone. This comprises an exhausted double-walled quartz cylinder B (Figure 11) fixed with sealing wax into the neck of a surrounding cylindrical glass vessel A, connected with an air pump by the tube F. The anode consists of an iron ring K, which surrounds the quartz cylinder and is suspended by means of two platinum wires fused into

[7] Ber. 1905, *38*, 2,630.

the walls of the glass vessel. Mercury is placed in the bottom of the latter to serve as cathode. The lamp is operated at 20 volts and 5 amperes and is started by means of an induction coil. Arrangements are made to cool the lamp both internally and externally, so that the temperature in the interior of the lamp is kept down, thus maintaining a low density of the mercury vapor, and favoring the production of ultraviolet rays.

A form of quartz tube mercury lamp recommended by Knipp[8] for bacteriological work is shown in Figure 12, which illustrates the tube and

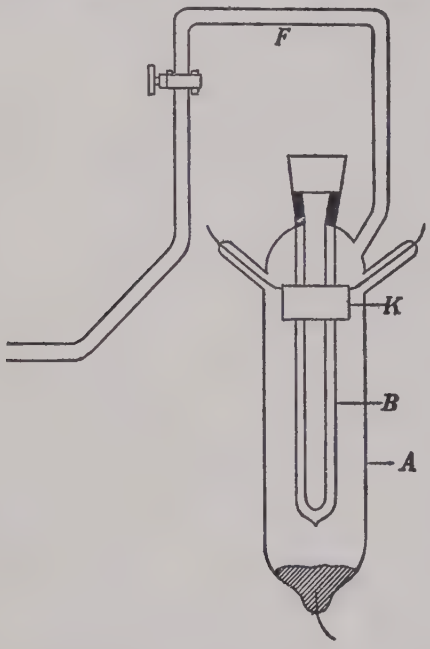


FIG. 11.—Fischer's Lamp for Formation of Ozone.

manner of mounting. The diameter of the main branch AB is 25 millimeters and the length of the straight portion 15 centimeters.

The tube is exhausted and barometric pressure depended upon for maintaining the mercury levels at A and B. This arc is suited only for low voltages and hence gives out comparatively weak ultraviolet radiations.[9]

Tian[10] describes a lamp made of a tube of transparent quartz down the center of which an insulated iron wire passes, thus making contact with a drop of mercury at the bottom, which forms the cathode. The anode is a small iron cylinder. Ordinarily direct current is used, but

[8] Phys. Rev. 1910, *30*, 641.
[9] A modified design remedies this to some extent.
[10] Compt. rend. *156*, 1063.

alternating current may be utilized if the anode is made double, i.e., two plates separated by a sheet of mica. This form of lamp has the advantage, besides low voltage operation, that it is of convenient shape to immerse in liquids.

A type of arc lamp using a mercury cathode and tungsten for an anode is proposed by Urbain, Seal and Feige.[11] Tungsten is employed because of its high melting point. It is necessary to operate either in vacuo or in an inert gas. When the smallest trace of oxygen is present the walls of the enclosing vessel became darkened through the production of volatile oxides. No noticeable transference of tungsten to the negative pole is observable.

FIG. 12.

A mercury vapor lamp manufactured by The General Electric Co.[12] consists of a carbon anode and a mercury cathode. A fine carbon filament runs through the lamp and dips into a cup which floats on mercury in the bottom of a tube. As soon as the current is started the cup is drawn down by means of a solenoid, thus forming an arc at the bottom of the carbon filament, and as this is more resistant to the current than mercury vapor the arc rapidly extends through the whole length of the tube.

The exposure of gases to ultraviolet radiation was carried out by Chapman, Chadwick and Ramsbottom[13] in apparatus of the form shown in Figure 13. A bulb of quartz, in which the gases are placed that are to be exposed to the rays, is enclosed in a glass mercury lamp of which the cathode is a pool of mercury and the anode a short cylinder of iron suspended in the upper part of the glass container. The latter is exhausted by means of a Sprengel pump. The quartz

[11] Compt. rend. 1911, *152*, 255.
[12] Child, Electrical Arc, New York, 1915.
[13] J. Chem. Soc. 1907, *91*, 945.

bulb has an outlet tube passing through the bottom of the lamp and communicating with a pump. The lamp is operated on a current of six amperes.

A lamp recommended by Coehn and Becker [14] for photochemical work and used by them in the oxidation of sulfur dioxide is shown in Figure 14. The lamp consists of a glass vessel 4 in which the double-walled quartz vessel 2 and 3 is placed. A mercury seal is used at the

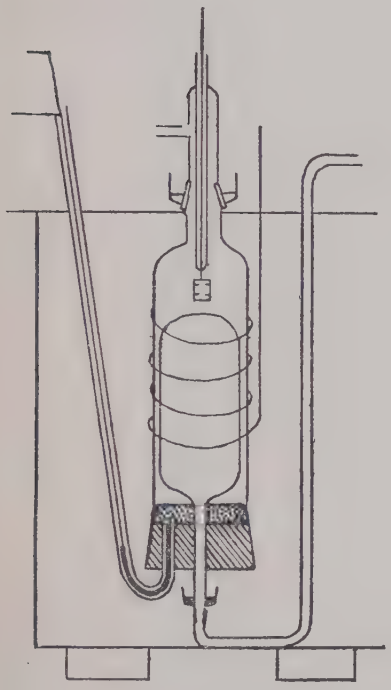


FIG. 13.—Gas Irradiation Apparatus.

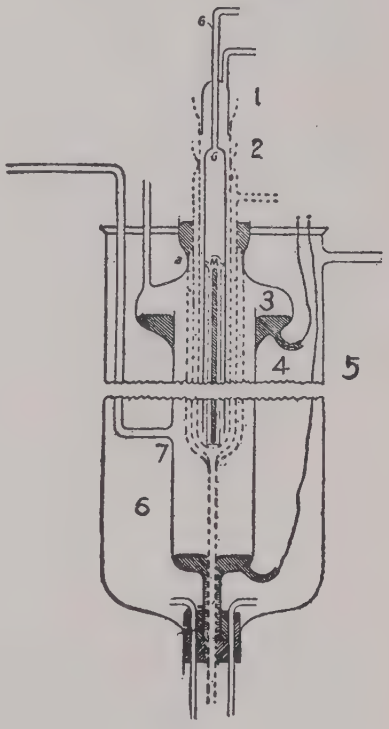


FIG. 14.

top of the vessel 4. The lamp is placed in a water-jacket or cooling vessel 5. In order to make the burning uniform a magnet M is placed in a glass tube in the lamp as shown. A quartz tube 1 is inserted in the vessel 2 through which gases may be passed by means of the inlet and outlet tubes G.

A lamp for technical applications of photochemistry is shown in Figure 15. A quartz tube K L A has a length of 115 centimeters. The light zone is maintained in the tube L, 1.8 centimeters in diameter. A tube R, 5 centimeters in diameter and 100 centimeters in length, is fused on the tube L. Reaction mixtures are passed in and out by the open-

[14] Zeitsch. f. physik. Chem. 1910, *70*, 90; Zeitsch. f. Elektrochem. 1907, *13*, 545.

ings Q, Q. The tube R is wound with nickel wire and jacketed with asbestos. The temperature is determined by thermo elements at N.

A quartz-jacketed lamp used by Weigert [15] especially for exposure of gases to ultraviolet rays has the form shown in Figure 16. A mercury arc is formed in the inverted U tube B, between surfaces of mercury E_1 and E_2, electrical connection being made at K_1 and K_2. M is a

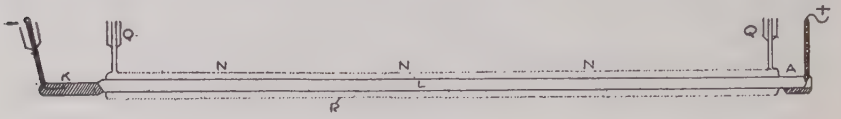


FIG. 15.—Lamp for Technical Applications.

mantle of thin quartz enclosing the burner. Capillary tubes of quartz, A_1 and A_2, are used for changing the gaseous atmosphere in the space about the burner. The apparatus is mounted in a watertight casing having a quartz plate serving as a window for external exposures.

The use of the mercury lamp in spectroscopy, polarimetry and saccharimetry is advocated by Lowry.[16] In spectroscopy no great intensity of light is needed, the light emitted from a vacuum tube being

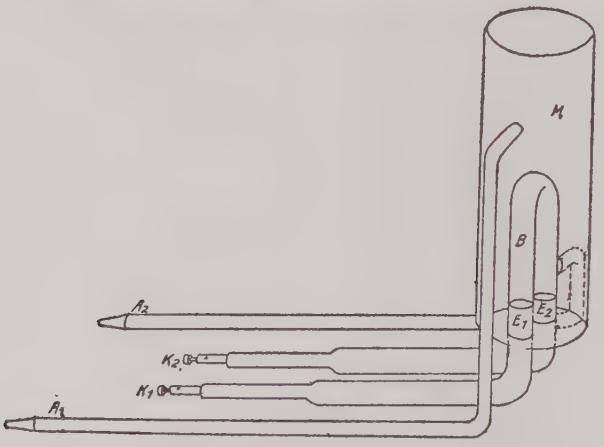


FIG. 16.—Lamp Employed by Weigert for the Treatment of Gases.

quite sufficient for taking readings with spectroscope or with an instrument such as the Pulfrich refractometer. A mercury light of sufficient intensity for this work, Lowry states, can be produced very conveniently from a hydrogen tube containing a globule of the metal; This hydrogen-mercury tube has the advantage that it lights more easily than a tube containing mercury only, while by warming the

[15] Zeitsch. f. physik. Chem. 1912, *80*, 69.
[16] Trans. Far. Soc. 1912, *7*, 267.

globule, the spectrum of the metal can be made as bright as may be wished.

The problem of providing a source of light for use in polarimetry (see page 67 on the use of the cadmium arc in polarimetry) is much more difficult, on account of the fact that the intensity of the light is reduced to a small fraction of its original magnitude by the action of the Nicol prisms. The polarizing Nicol begins by eliminating half the light, and if the half-shadow angle of the instrument is set to 5° there is a further reduction to ½ sin 2½° = 0.0218 at the "extinction" position. The intense light of the modern mercury lamp renders it exceptionally suitable for use in polarimetry, and it is now beginning to be employed to a considerable extent also in technical saccharimetry. The chief advantages of the mercury light may be summarized as follows: (1) The green light is of exceptional purity; a high rotatory

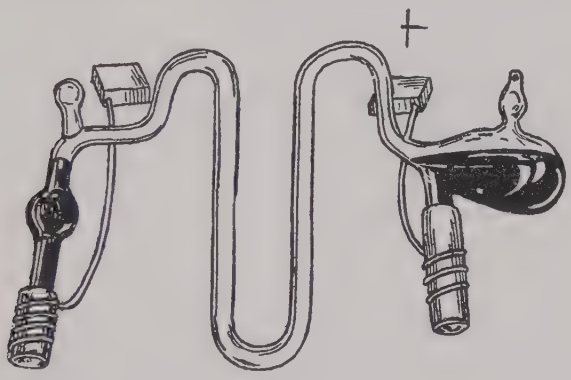


FIG. 17.—The Bastian Glass Mercury Lamp.

power can be read as easily as a low one; on the other hand, when sodium is used, the two lines, D_1 and D_2, do not extinguish together except in the case of small rotations. (2) The line can easily be separated from the other constituents of the spectrum by means of a direct vision prism of low power; no extra cost is involved in fitting this to the eyepiece of the polarimeter, as even sodium light cannot be used for accurate work unless some such method is used to purify the crude flame-spectrum. (3) On account of the great intensity of the light the half-shadow angle of the polarimeter may be reduced to 2°, 1° or less; the instrument then becoming exceedingly sensitive. Alternatively, cloudy or colored sugar syrups may be read with a half-shadow angle of moderate size. (4) The light is absolutely steady and may be kept running without interruption for a week at a time; all risk of change of zero through changed illumination is thereby avoided. (5) Contamination of the atmosphere and dirtying of the instrument by sodium salts are avoided. (6) The readings are usually at least 18 per cent greater for mercury green than for sodium yellow light.

The credit of introducing the use of the mercury lamp in polarimetry, according to Lowry, belongs to Disch [17] and to Schonrock [18] who made use of the Arons lamp. In 1906 Lowry introduced this method of illumination in his own laboratory and since that date has discarded the sodium light, except when dispersion values are required, or when some comparison has to be conducted with observations made by the older methods.

Although no longer on the market, the Bastian glass mercury lamp (Figure 17) is recommended by Lowry for ordinary laboratory use. Its current consumption is small; no auxiliary resistances are required; the cord carrying the current to the lamp can be plugged into the ordinary lighting circuit without damaging the wires or blowing the fuses; and for work of high accuracy the light is found to be purer, and the continuous background to the spectrum far less intense, than

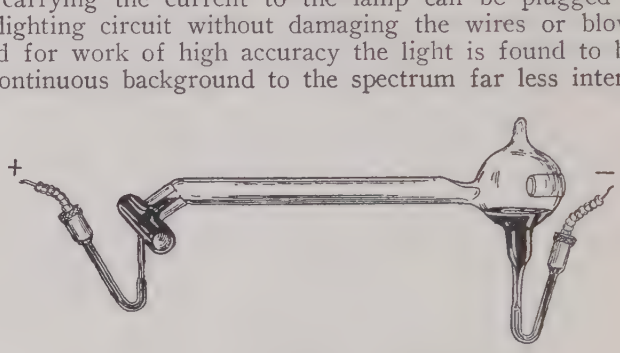


FIG. 18.—Lamp Used in Polarimetry.

in the case of the quartz lamps of high power which have displaced it in commercial use. The lamp is intended to burn with the zig-zag tube in a horizontal plane; but as soon as the tube is hot it may be turned into a vertical plane and will burn in this position for some days without going out. It is then possible to focus one of the straight portions of the tube upon a vertical slit, thus producing an intense and uniform linear illumination. Two forms of quartz lamp have been designed for use with the polarimeter. The lamp shown in Figure 18 was constructed in order to use the arc in the end-on position. In a lamp of this type the bulb on the right in the figure usually becomes covered with drops of condensed mercury.[19] To avoid this

[17] Ann. Phys. 1903 (iv), *12*, 1155.

[18] Z. Vereins Deutsch. Zucker, Ind., 1903, *53*, 652.

[19] A form of the Bastian or Quartzlite lamp described by Perkin (Trans. Faraday Soc. 1911, *6*, 199), consists of a straight tube about one quarter inch in diameter and six inches long, and has a tantalum button as anode. The negative end terminates in a bulb containing mercury, and the positive end also has a smaller bulb of mercury which makes contact with the tantalum. Owing to the tantalum button being raised to a bright red heat a certain quantity of red rays are furnished, which to some slight extent neutralize the peculiar violet of the mercury. The important action of the tantalum, however, is to cause continuous burning once the lamp is started by tilting. The arc at the positive end does not play from the mercury but from the tantalum, consequently no mercury distils over to the negative pole. Further, owing to the large reservoir of mercury at the negative end, it is kept comparatively cool, and no special radiating surfaces are required.

a window of polished silica was mounted on a re-entrant tube in the center of the bulb where it is kept hot by the arc and remains clear and free from globules of mercury. The lamp takes a current of 3½ amperes and produces a very powerful light. It was found to be of very great service in taking polarimeter readings with the violet mercury line, when studying rotatory dispersion; the violet light being so intense that readings can be taken with a half-shadow angle of about 4° only. The chief disadvantage of the end-on lamp is that a slight displacement of the lamp may produce a marked alteration in the relative illuminations of different parts of the field of the polarimeter. The lamp must therefore be set very carefully if a con-

FIG. 19.—Vertical Type of Lamp.

stant zero-reading is to be maintained. The difficulty can be avoided by using a horizontal line of light to illuminate the polarimeter when the field is divided vertically, or a vertical line of light for a polarimeter in which the divisions are horizontal. Most of the commercial quartz mercury lamps are arranged with a horizontal arc, and are therefore not suitable for use with a spectropolarimeter in which the division of the field must be made horizontal. In order to overcome this difficulty the lamp shown in Figure 19 was devised. It is a modification of the commercial "Quartzlite" lamp and was constructed especially for use in the vertical position. The line of light is very intense as the arc "pinches" into a narrow column (about ⅛ inch diameter) in the center of the tube. The only drawback to this concentration is the development of an appreciable quantity of continuous light, and a marked intensification of the weaker lines, demanding some additional care in the spectral purification of the yellow and violet lines.

At the time when there were no suitable quartz mercury-vapor lamps on the market in this country Bovie [20] required a source of ultraviolet rays for certain biological and photochemical investigations. He constructed quartz lamps which after four years of use still gave excellent results. The lamps are not difficult to make and the design of this "home-made" apparatus can be altered to suit particular requirements. Figure 20 shows a simple form which the lamp may take.[21] A is a quartz tube one centimeter in diameter. One end is bent downward to form the positive electrode C. A quartz tube of the same diameter is sealed in, near the other end, to form the negative electrode B. The distance between B and C is about 10 centi-

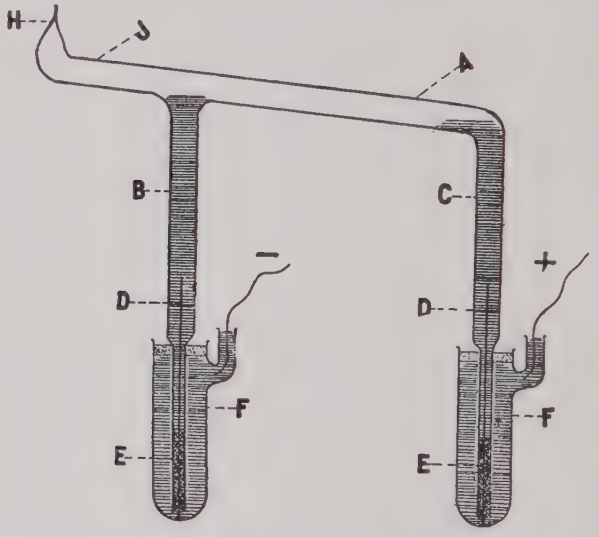


FIG. 20.—Lamp Used by Bovie for Biological Work.

meters. The end of the tube A forms a condenser. The lamp is sealed, after exhausting at H. The tube A should be inclined to the horizontal position at an angle of 6° to 7°, the end J being higher, so that the condensed mercury will flow back into C. Pieces of five millimeter quartz tubing are sealed to the lower ends of B and C. These in turn are set in mercury cisterns F, F (made of glass); test-tubes may be used. The small tubes are sealed at E. The detail of the seal is shown in Figure 21. A bulb of wax on the outside is necessary in order to make the seal air-tight. The iron wire D conducts the electric current through the wax seal.

The lamp should be used on a 110 volt direct current with five or six sixteen candle power bulbs in multiple as resistance, and will

[20] J. Biol. Chem. 1915, 315.
[21] The form of this lamp is copied from a lamp made by Kraus.

carry from 1.25 to 1.5 amperes, depending upon the amount of cooling at the electrodes B and C.

Figure 22 shows another of the possible forms of the lamp. It will be seen that the tube A is vertical. The electrode C, which is left open at the bottom, dips into a cistern of mercury M. This lamp was designed to run on a 220 volt circuit, and the distance between B and C is 30 centimeters. The lamp, however, will work as well on a 110 volt circuit; for the distance between C and B is easily adjusted.

The condenser J is not in a line with A, but is a little to one side. This is important, for a certain amount (about half) of the condensed mercury must be returned to the electrode B, else it will boil dry. The condenser J and the electrode B are provided with copper radiators, K. The lamp can be made to carry a current of four amperes,

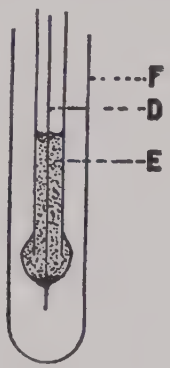


FIG. 21.—Construction of Seal.

and with this current density and with an arc 30 centimeters long the lamp emits an abundance of ultraviolet rays.

A more powerful lamp is described by Bovie.[22] The principles of the mercury air-pump have been incorporated into the design so that no pump, other than an ordinary water aspirator, is required to exhaust the lamp to a very high vacuum. This feature not only does away with all troubles connected with the original exhaustion of the lamp, but makes it possible to re-exhaust the lamp quickly and easily at any time. The lamp can be re-exhausted without in any way disturbing the chemical substances under investigation and without interrupting the exposure for more than a fraction of a minute.

The lamp, Figure 23, is operated on a direct current in series with a resistance, which, for voltages above 110, should be variable. It carries a current of from 12 to 15 amperes. The maximum length of arc obtainable is dependent upon the voltage of the line upon which the lamp is operated. With 110 volts on the line, an arc of about 9 inches can be maintained. With 220 volts, the lamp burns with an arc over

[22] J. Am. Chem. Soc. 1915, *37*, 1721.

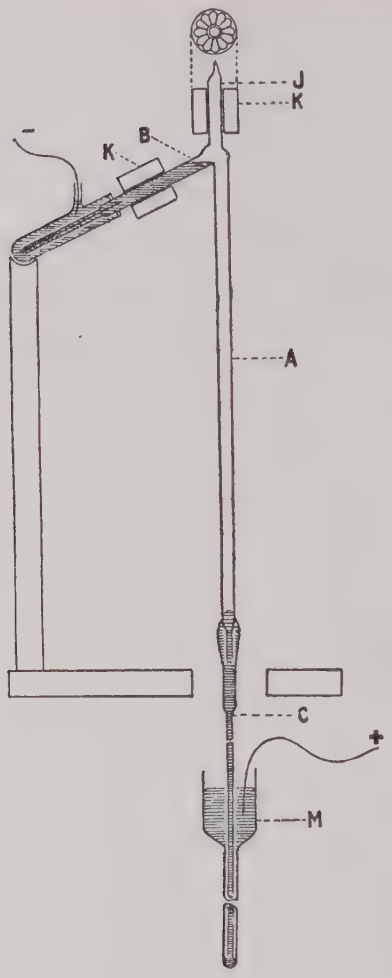


FIG. 22.

FIG. 23.

two feet long. It is essential that the mercury column be made the positive electrode; the lamp will not burn if the poles are reversed.[23]

A mercury vapor lamp with quartz illuminating tube is described by Gallois.[24] In the initial position the mercury fills the illuminating tube, but when the current is started, a coil attracts an armature connected by a rod with the tube, and turns the latter on its axis about

[23] Data on the expansion of fused quartz are given by Henning (Ann. Physik. 1903 (iv), 10, 446; J. Chem. Soc. 1903, Abs., 84, ii, page 272) for temperatures up to 1000°. It is found that the mean increase of unit length for a rise of 1° is 0.00000054.

[24] Bull. soc. encour. ind. nat., 121.

40°, whereby in consequence of the shape of the tube the mercury is divided into two portions and an arc is formed across the intervening space. Quartz lamps are constructed to work under tension of 220 to 500 volts, giving a candle-power of 500-6600.[25]

According to Weigert [26] the quantitative study of photochemical gas reactions under the influence of ultraviolet radiation is rendered difficult by the temperature effect produced when the lamp is in action. Attempts to avoid this by water cooling usually involve the passage of the radiation through a layer of water where it is largely absorbed. In Weigert's apparatus, which is water cooled, the reaction takes place in a vessel outside the lamp itself, but the reaction vessel receives radiation which has only passed through such non-absorbing media as quartz and hydrogen. Henri,[27] as a result of experiments on the ultraviolet radiation from a mercury vapor lamp demonstrated that the radiation becomes more intense as the temperature of the luminous tube is allowed to rise. By cooling the tube with water, the radiation was found to be 14 times less powerful than with air, the same number of watts being consumed. The yield seems to depend on the fall of potential in the luminous tube. Quartz mercury vapor lamps have proved to be a very constant source of ultraviolet rays and one in which the radiation is definite when the voltage, amperage and length of the tube are known. Thompson [28] states that for the purpose of sterilizing water and other liquids it is preferable to keep the vapor pressure in the mercury lamp employed as low as possible; hence the electrode-containing cells must be efficiently cooled. On the other hand in order to avoid undesirable contact between the quartz globe of the lamp and the liquid, a quartz jacket is employed and the space is exhausted. In the lamp proposed by Thompson, the quartz jacket does not extend to the electrode-containing cells at the end of the lamp, but is connected to the illuminating tube between the cells. The electrodes are thus kept cool by the liquid which is being sterilized or in case the liquid is hot, some external means of cooling is used. The procedure serves to keep the vapor pressure of the mercury low. Perkin [29] has designed a lamp for experimental purposes which is constructed of fused quartz, and so arranged that gases can be circulated through it. The lamp consists of a quartz tube 3.5 inches long, which terminates at either end in mercury reservoirs, electrical contact being made by means of platinum wires, passing into the mercury. The tube is exhausted and the arc is struck in the usual manner by tilting.

It is stated by von Recklinghausen, Helbronner and Henri [30] that in a mercury vapor lamp of given dimensions using a constant amount of electrical energy there exists a definite relation between the amount

[25] Some of the structural details of the quartz mercury lamp together with the difficulties experienced in developing it are given by Pierce, Illuminating Engineer, N. Y., 1911, *6*, 133.
[26] Z. physik. Chem., 1912, *80*, 67.
[27] Compt. rend. 1911, *153*, 426.
[28] British Patent 28,757, December 20, 1911.
[29] Trans. Far. Soc. 1918, 199.
[30] U. S. Patent 1,176,481, Aug. 29, 1916.

of ultraviolet rays produced and the amount of luminous radiation. If, however, any of the above conditions are changed, the ratio between the ultraviolet and luminous portions of the radiations will be altered. This is probably due somewhat to the temperature of the lamp as the ultraviolet rays are increased in a given length of tube as the temperature rises. By constructing the mercury vapor chamber in the form of a U the two electrodes are brought close together and the heat radiations from one help to heat the other, thus raising the amount of ultraviolet rays produced in proportion to the current consumed. In the construction of lamps of the U shape, there is a tendency for that portion of the quartz tube at the bend to deteriorate or become opaque due to the fact that in making this bend the center of the tube is not followed by the arc. It is proposed to reinforce these U shaped tubes on the inside of the bend, thereby prolonging

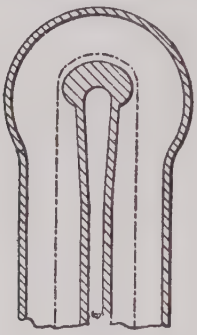


FIG. 24.

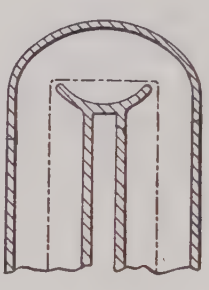


FIG. 25.

their life. In a form of lamp devised by Helbronner and von Recklinghausen [31] the lamp proper is surrounded by a quartz envelope. The air is completely exhausted from the space between the lamp and the outer tube or envelope so that, when the apparatus is immersed in a liquid, radiation of heat from the lamp is prevented, while the normal working of the lamp is not affected. The wires conducting the current to the lamp pass through the walls of the envelope. In one form only the straight tube between the two bulbs is surrounded by an outer jacket.

Although the U shaped type of lamp is productive of a greater proportion of ultraviolet rays, probably due to the increased heating effect resulting from the proximity of the two arms, tubes of uniform bore are not entirely satisfactory. It is found that the operating life of these lamps can be considerably increased by providing arrangements intended to determine to some extent the path of the luminous arc, devices of this kind being illustrated in Figures 24 [32] and 25.

The luminous arc naturally tends to take the shortest path from one

[31] British Patent 14,129, June 10, 1910.

[32] U. S. Patent 1,271,246, July 2, 1918, to von Recklinghausen, Helbronner and Henri.

electrode to the other and it necessarily follows that with a lighting tube of U shape the luminous arc instead of traversing the middle of the tube as in the case of a straight lighting tube, tends to approach that side of the curved portion of the lighting tube which is adjacent to the center of curvature, following in fact the dotted line indicated in Figure 24. The inner face of the lighting tube is thus exposed by reason of the extremely high temperature of the luminous arc, to much more rapid deterioration than the other portions of the tube and the corrosion thereby effected is found after the expiration of a certain time, to cause the wall of the lighting tube at this point to become somewhat porous and permit the entrance of air, rendering the lamp inoperative due to the vacuum being impaired. This disadvantage is obviated by the arrangement shown in Figure 24 in which the injurious effect is counteracted by making that

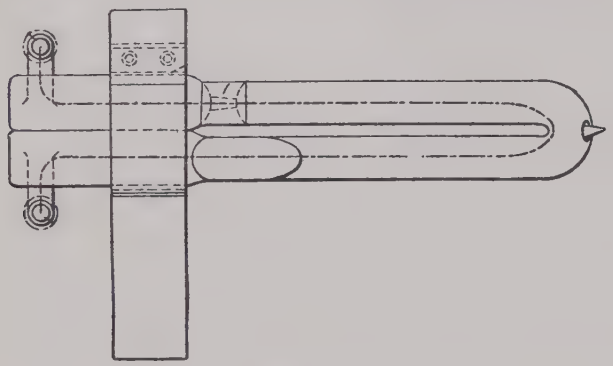


FIG. 26.

portion of the lighting tube of considerably increased thickness. The quartz wall being thickened at this point can readily resist without injury the action of the high temperature of the luminous arc. A modified arrangement for the same purpose is illustrated in Figure 25, in which in order to maintain the luminous arc away from the wall of the lighting tube a number of projections are provided; the dotted line indicates how the luminous arc is kept at a certain distance away from the wall of the lighting tube.

Figure 26 shows a mercury vapor lamp comprising a quartz tube of U shape, the two arms of which are very nearly in contact. The internal form of the lamp is such as to provide a restricted portion shown in Figure 27 adjacent to the negative electrode, while the lamp tube is flattened adjacent to the positive electrode. Fragments of broken glass are placed between the restricted portion and the terminal. Similar fragments are placed between the flattened portion and the terminal of that arm.

The effective life of a quartz mercury vapor lamp is increased by von Recklinghausen [33] through reinforcing the quartz tube at the points

[33] U. S. Patent 1,188,587, June 27, 1916.

which are subject to the greatest deterioration. See Figure 28. There is a certain spot in lamps of the usual construction which von Recklinghausen calls the "cathode spot," at which point the concentration of the current and the exceedingly high temperature produced have a tendency to disintegrate or otherwise injure the quartz surface. As

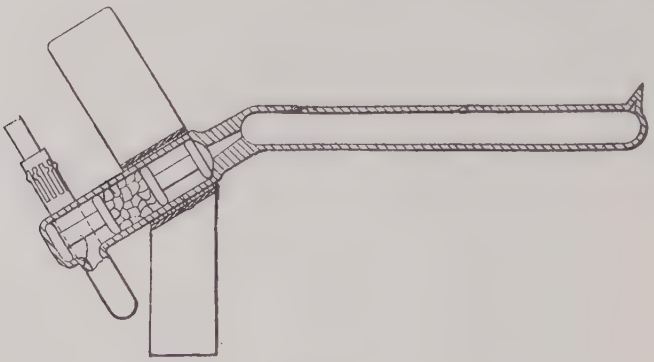


FIG. 27.

a remedy for this, von Recklinghausen proposes to line this portion of the quartz lamp with a highly refractory material such as "titanium zircon quartz" and thus to greatly prolong the life of the lamp. Inasmuch as this "cathode spot" does not remain stationary but is advanced or retarded according to the workings of the lamp, quite a consider-

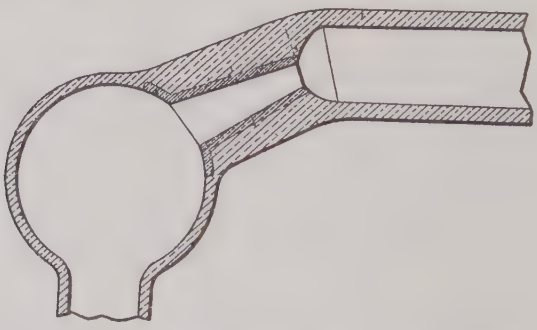


FIG. 28.—Von Recklinghausen Lamp Reinforcement.

able portion of a constricted surface as well as a portion of the condensing bulb is lined with this material. It is claimed that cracking and clouding of the quartz is obviated to a great degree by this method of construction.

A design of a mercury vapor lamp yielding nearly cold light is described by Daguerre, Medard and Fontaine [84] which is in the form of

[84] Compt. rend. 157, 921, 1914.

an inverted U tube and is made of fused silica. Electrodes of invar enter the ends of the tube. A short intense arc is formed at the bend of the tube between the columns of mercury on either side. The lamp is enclosed in a transparent silica flask—the wall of which is paraboloidal and silvered to act as a reflector—and is immersed in a tank of water. The light is concentrated by the mirror and emerges through a silica window in the tank. The lamp consumes 18 amperes, either alternating or direct current, at 70 volts and yields 3,000 candle power. The light can be used for microscopy and projection work without heating the specimens or celluloid films. It has the advantage over the carbon arc

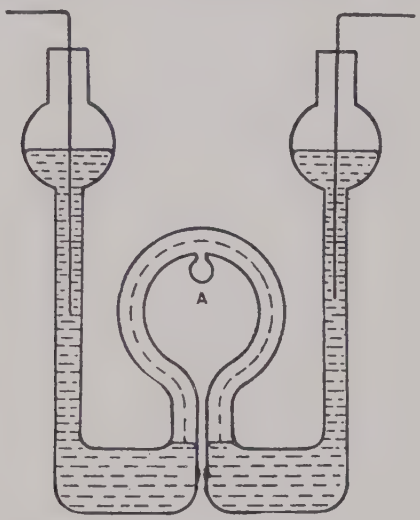


FIG. 29.—Kent and Lacell Lamp.

in that the luminous point remains fixed and requires no regulation. Its application to water sterilization and submarine photography has been suggested.

An extremely powerful lamp devised by Kent and Lacell has a U shaped quartz tube and will work on a 500 to 1000 volt circuit (Figure 29). One of the difficulties in causing mercury vapor lamps to burn continuously is the fact that the anode end becomes heated to a higher temperature than the cathode. Consequently there is a tendency for the mercury to distil from the hotter anode to the cooler cathode. Kent and Lacell overcome this difficulty by bending round the quartz tube so that the anode and cathode are adjacent, and the heat from the anode raises the temperature of the cathode. In consequence of this heating of the negative electrode, the two electrodes automatically adjust themselves to about the same temperature. Consequently when once the arc is started through the mercury vapor there will be no greater tendency for mercury to be lost from the lamp, working at a constant pressure of mercury vapor, because the space in which the arc is formed

is saturated with mercury vapor at the working temperature and the arc remains constant.[35] An interesting point in connection with this lamp is that it is not evacuated. The lamp is started by heating electrically a small coil of wire placed round A. When the lamp has started, the current is automatically cut off from A.[36]

Among the various types of ultraviolet lamps Cooper-Hewitt [37] suggests a vapor lamp employing metals such as thallium and cæsium in order to increase the ultraviolet efficiency. In the construction of this lamp, mercury is used in one end of the quartz tube and acts as the anode, while the other metal is placed in the opposite end of the tube and serves as the cathode. Inasmuch as thallium and cæsium are solid at ordinary temperatures and difficulty would be experienced in starting the lamp, in case it were handled in the same manner as a quartz mercury lamp, a connecting rod is inserted between the mercury and the cathode to assist in starting the lamp. When a heavy current is turned on, the cathode is heated to such an extent that the metal becomes molten and partially vaporized, after which the operation of the lamp takes place in the usual manner. A Cooper-Hewitt lamp of a different type [38] has a positive electrode of iron and a negative electrode of mercury.

Perkin [39] furnishes a description of a quartz lamp devised by Cooper-Hewitt. The arc is struck in a highly exhausted quartz tube by tilting so that mercury makes contact with mercury, and then breaking contact. The anode end of the tube consists of a bulb into which the mercury vapor condenses, thus preventing rise in pressure and any tendency to intermittent burning. These lamps are made to burn on 200-250 and 100-130 volt circuits. The mean specific consumption of energy on a 220-volt lamp is 0.22 watt with an illuminating power of 3,630 candle power.[40]

A mercury vapor lamp of the Heræus type used by Foster [41] is shown in Figure 30. The essential part is a small bore tube A, of quartz, bent into U-shape with the arms close together. The upper ends are bent over and end in bulbs which are filled with pure mercury up to the level shown. Platinum contact wires pass down two other tubes which are sealed into the bulbs at the back. The bulbs, inlet tubes for the wires, and part of the U-tube are all enclosed in a brass casing C, which has a glass front not shown in the sketch. The projecting part of the U-tube is enclosed in a thin-walled quartz tube B, which is cemented into brass casing. Close behind the U-tube a nickel tube enters, through which water flows. The water fills the whole of B and C and is carried away by another tube at the top, so that a

[35] British Patent 21,834, 1908.
[36] Perkin, Trans. Far. Soc. 1911, 6, 199.
[37] U. S. Patent 1,197,629, Sept. 12, 1916.
[38] Elektrotechnische Zeitschrift 1905, *26*, 941.
[39] Trans. Far. Soc. 1911, *6*, 199.
[40] Garnier, L'Electricien 1910, *39*, 133, discusses the applications of the mercury vapor lamp and the development of the Cooper-Hewitt lamp together with a number of calculations of temperature and other theoretical observations.
[41] J. Chem. Soc. 1906, *89*, 913.

water-jacket surrounds the lamp and keeps it quite cool. The lamp is lighted by inverting it slowly so that the two threads of mercury in the U-tube meet at the bend. On turning the lamp in the reverse direction, the arc is struck, and fills the whole of the U-tube up to the mercury bulbs. A starting resistance is necessary owing to the momentary short circuit which occurs when the mercury threads meet. The lamp requires

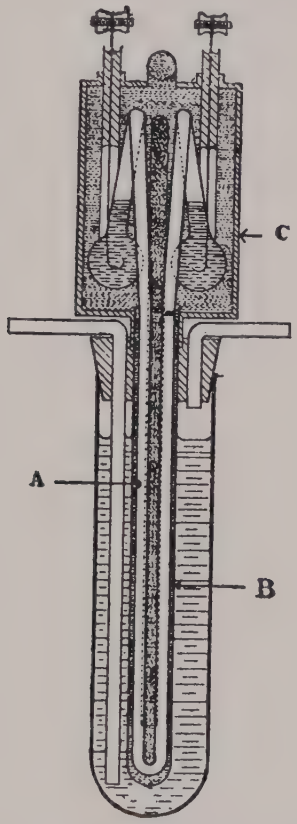


FIG. 30.—Foster's Apparatus.

230-240 volts, and uses 5-6 amperes. Axmann [42] describes a simple ultraviolet lamp consisting of a uviol glass tube 45 to 130 centimeters long having platinum lead-in wires and carbon points. A quantity of mercury is placed in the tube. The lamp operates at 110-220 volts, 2-4 amperes.

The initial ignition period of a quartz mercury vapor lamp is reduced by employing a smaller amount of mercury than is ordinarily employed.[43]

[42] Elektrotechnische Zeitsch. 1905, *26*, 627 and 1182.
[43] British Patent 165,081, May 12, 1921; J. Soc. Chem. Ind. 1922, *41*, 742-A.

A self-exhausting mercury vapor lamp is described by Wonan.[44] The gases are expelled by the use of mercury contained in a side tube. A mercury vapor lamp devised by Harrington [45] will operate on 25 volts direct current, yielding a brilliant light of capillary tube dimensions.

Ultraviolet lamps containing argon, helium and neon have been used advantageously by Bayle, Fabre and George.[45a] These are of three types (1) A d.c. quartz mercury lamp having an atmosphere of argon at 500 mm. mercury. The arc strikes instantaneously upon application of the voltage and the lamp automatically relights if it should happen to be extinguished. Its steady state is reached in a much shorter time than that required by the ordinary rocking type of lamp. (2) A 2 kilowatt a.c. arc of 60 cm. length using 3000 v. An atmosphere of argon, helium or neon at about 1 mm. mercury is used. And (3) a less powerful (400 w.) high tension arc using gaseous atmosphere and a high-frequency a.c. (750 kilocycles). The gas arcs give a more brilliant and a stronger continuous spectrum than the ordinary arc for equal amounts of power. The latter gives the same spectrum as the former if 1.66 times as much power is used.

A mercury vapor lamp of the Cornu type [46] is so arranged that the mercury of the cathode cannot be displaced, but the anode mercury, cooled by a condensation chamber, may be slowly displaced by passing through a valve intended to damp its oscillations, the pressure inside the lamp being always, even in a cold state, greater than atmospheric pressure. The cathode section is formed by a tube, which is in connection with the negative pole of the current supply and united to a cooling chamber connected by a thick-walled bent quartz tube to a condensing chamber. A valved tube, forming a part of the anode section, is in connection on the one side with the condensing chamber and on the other side with the positive pole of the current supply, through the medium of a spiral-shaped conductor exerting pressure on the valve. The meniscuses of mercury may be separated for striking the arc by means of a gas heater under the quartz tube, or by a capillary tube connected to a pump for introducing nitrogen, argon, etc., at the highest point of the quartz tube, or by means of an expansion bulb containing a heated filament and filled with gas, connected by a capillary tube to the quartz tube. A mercury arc lamp is described by Heræus [47] which has a tungsten anode placed at such a distance from the mercury as to maintain permanency of the arc even at high pressures and with great resistance. In this lamp a ten-fold increase in brightness corresponds to a twenty-fold increase in the ultraviolet radiation in the neighborhood of 366 μμ (3660 Å) and there is smaller consumption of energy and a more permanent length of arc than with carbon arc lamps. A quartz mercury vapor lamp which operates on alternating current is

[44] J. Sci. Instruments 1923, *1*, 54; Chem. Abs. 1924, *18*, 1088.
[45] J. Optical Soc. Am. 1923, *7*, 689; Chem. Abs. 1924, *18*, 356.
[45a] Bull. soc. chim., 1925, (4), *37*, 89; Rev. d' optique 1925, *1*.
[46] British Patents 129,022, 129,702, 1917; U. S. Patent 1,343,037; J. Soc. Chem. Ind. 1919. 622-A.
[47] J. Soc. Chem. Ind. 1920, *39*, 566-A; German Patent 318,836, 1918.

described by George.[48] A quartz tube is connected at each end by a thick walled, narrow bore tube with a spherical mercury container having an inner spherical bulb communicating with it by a small hole on the side opposite the quartz tube. The electric wires pass into the inner spherical chamber. The quartz tube is filled with an inert gas under pressure which acts as a conductor for the current until enough of mercury is vaporized.

In another mercury vapor lamp described by George [49] a small tube is joined to the top of the vessel containing mercury vapor and extends downwards within the vessel nearly to the bottom. The lower portion of the positive terminal, in the form of a helix of tungsten wire, is disposed in this tube, its extreme lower end being immersed in the mercury. A double walled quartz mercury vapor lamp made by the Quartz Lamp Co., Hanau,[50] is primarily adapted for use for medicinal purposes, but may also be used for sterilization of milk and water, and in the preparation of patent leather and artificial rubber. Nutting's mercury arc lamp [51] has an anode and a cathode leg, and a connecting arc tube formed of hard glass softening only at a high temperature, the tungsten leading-in wires and terminals being sealed into the ends of the legs. Podszus [52] proposes a type of metallic vapor arc which will burn steadily and continuously in any atmosphere. The lamp consists of a large globe of glass or quartz open at the bottom and fitted with a narrow exit tube at the top. The wide opening at the bottom stands in an iron receptacle containing mercury. Through the bottom of the receptacle are three openings. A narrow glass tube for admitting gas passes through the first; the second opening admits the cathode, and the third the anode. The cathode is made of iron and down the middle of it a tube of boron nitride passes. Covering the top of the cathode is a plate of tungsten perforated by a narrow opening in the center. The object of the boron nitride and the tungsten plate is to stabilize the arc and to prevent fluctuations of the mercury of amalgam which constitutes the cathode. The anode is a tungsten rod. The arc is struck by lowering the anode until it touches the cathode and then drawing it away. The arc produced is a thin, quiet flame, which is affected in color by the gases in the globe and by the metal used as cathode. In hydrogen the light is greenish white; in nitrogen bluish-white.

Sand [53] claims that zirconia neither affects the spectrum nor, if properly introduced, does it shorten the life of the cadmium-vapor arc lamp, in case the material is thoroughly dehydrated before use. Other-

[48] J. Soc. Chem. Ind. 1921, *40*, 75-A; U. S. Patent 1,361,710.
[49] U. S. Patent 1,398,545.
[50] von Heygendorff, Z. angew. Chem. 1920, 33, 1, 243.
[51] U. S. Patent 1,320,087.
[52] Zeitsch. Elektrochem. 1917, *23*, 179.
[53] Phil. Mag. 1920, *39*, 678; Chem. Abs. 1920, *14*, 3601. Note Electrical Review West Elec. *67*, 654; Chem. News 1915, *112*, 151. The cadmium is freed from oxide and dissolved gas by filtration and exhaustion. The metal is melted by external heating before starting. Zirconia as a loose powder is added to hinder the adhesion of the metal to the walls.

wise the water vapor may cause a cadmium glass to be formed. According to Bates [54] one of the difficulties in using the cadmium arc quartz lamp as a source of monochromatic light is the adherence of pure cadmium, upon solidification, to the quartz wall with such tenacity as to destroy the lamp. Attempts to overcome this by introducing mercury to form a softer alloy were successful as far as protection of the quartz goes, but the mercury does most of the conducting and the cadmium lines are too faint to be of use. Pure gallium has been substituted for mercury with success. A mixture of cadmium with gallium is distilled under a pressure of 0.001 mm. into the quartz lamp, which is then sealed off. Enough gallium is carried over to give an alloy which does not damage the lamp. Such a lamp has been in use for over a year and apparently with proper care should last indefinitely, as the cadmium spectrum is as bright as when pure cadmium is used. The red line of cadmium 643.9 μμ (6439 Å) should be particularly useful as a source of monochromatic light as there has previously been no strong source in the visible red region. According to Wolfke [55] electrodes of cadmium-mercury amalgam (10% mercury) give no more of the characteristic mercury radiation than the carbon arc.[56, 57]

To improve the vacuum in electrical apparatus, especially as applied to the quartz mercury vapor lamp, von Recklinghausen [58] suggests the use of certain metals which have the property of absorbing nitrogen when heated to a high temperature. For this purpose magnesium, boron and titanium are proposed, the latter two being preferred. The nitrogen-occluding metals are introduced into the chamber in a solid or powdered form and means provided for raising them to the desired temperature. For example, in the construction of a mercury vapor lamp the nitrogen-occluding metals are placed either in a small tubular projection blown in the vessel or they may be used in the form of bars and connected with an electric current. The mercury is placed in the chamber and the vacuum drawn in the usual way. Before setting the lamp in operation the nitrogen-occluding metals are heated and in this manner the normal vacuum is increased. In case there is a leak in the vacuum seals allowing a small quantity of air to enter, thus decreasing the vacuum, it is claimed that the heat generated by the operation of the lamp will raise the

[54] Bur. Standards, Sci. Paper 1920, *371*, 45; Phil. Mag. 1920, *39*, 353; Chem. Abs. 1920, *14*, 1937.

[55] Elektrotech. Z. *33*, 917. Note also Illuminating Engineer, London, 1912, 5, 476.

[56] A description of a simple lecture apparatus for demonstrating the properties of the infra-red and ultraviolet parts of the spectrum has been given by Houstoun, Nature 1920, *105*, 421.

[57] Berlemont (Bull. soc. encour. ind. nat. 1921, *133*, 254; Chem. Abs. 1921, *15*, 2163) in collaboration with George and others, has made a lamp for medical and experimental uses in which tungsten is employed and the arc is not formed in a vacuum but at atmospheric pressure. The quartz lamp easily stands at the head of the list of artificial light sources for photographic work. (Electrical Review and Western Electrician 1910, *57*, 971). A large number of tests show that the operating life of the mercury rectifier varies between 205 and 1852 hours, depending largely upon the freedom from grounds, surges and wide current fluctuations (Anon. Elec. Rev. 1919, *75*, 668).

[58] U. S. Patent 1,110,576, Sept. 15, 1914.

nitrogen-occluding metals to a temperature at which they will readily absorb the air which has entered the lamp due to leakage and thereby maintain the vacuum automatically. (See Figure 31.) The proper distribution of the conducting fluid, in a mercury vapor lamp has been investigated by von Recklinghausen [59] who states that it is customary in some cases to use a series of electrodes in lamps of this type and that in these cases difficulty is encountered in maintaining the proper distribution of the mercury. In order to obviate these difficulties von

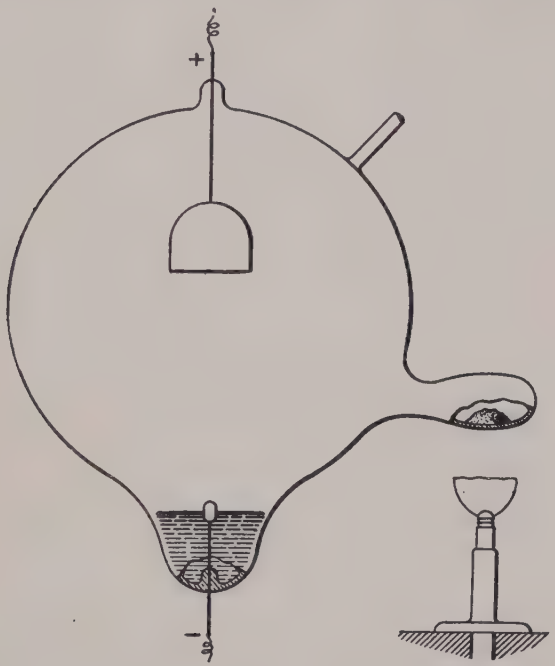


FIG. 31.—Von Recklinghausen Nitrogen-Absorbing Lamp.

Recklinghausen proposes the inclining of the arc container, the condensing chamber being located at the top. The condensed metal flowing along the bottom of the tube fills each pocket in succession, the remaining metal overflowing and running along down the tube until the next electrode is reached. This pocket in turn is filled in case it is not already full, the overflow passing on to the next electrode. In an operation of this kind difficulty might be encountered, causing a short circuit, in case the entire bottom of the tube was covered with a stream of mercury. If, however, a wire is placed at the upper edge of the electrode pocket, the mercury will accumulate and flow intermittently from one pocket to the next, thus breaking any contact which might otherwise be formed. (See Figure 32.)

[59] U. S. Patents 1,091,244, March 24, 1914, and 1,110,574, September 15, 1914.

Another type of apparatus using the same method of maintaining the mercury distribution consists of an arc container having two tubular extensions on the bottom side which dip into vessels containing a supply of mercury. These two vessels are connected by means of a small pump in order to transfer mercury from one vessel to the other. The positive pole is connected through one of these containing vessels, the negative pole being connected to the quartz chamber through an electrode pocket. As the metal is vaporized it condenses and flows into the electrode pocket and from here overflows and runs down into one of the chambers. An excess or deficiency of mercury may be corrected from the receiving vessels. As in the previous type short circuits are prevented by placing obstructions just in advance of the electrode pockets. Bachmann [60] claims to eliminate the defect in the mercury vapor lamp arising from

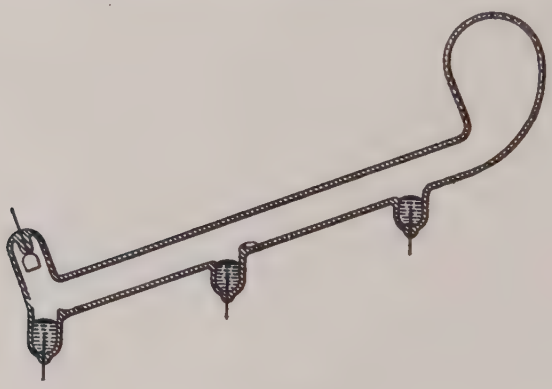


FIG. 32.—Lamp with Arc Container in an Inclined Position.

evaporation of the mercury by the use of an anode of metal or alloy, the surface of which is amalgamated anew from time to time by means of mercury supplied from near the electrode. In order to produce vacuum tight joints between the leading-in wires and quartz material Heræus [61] uses wires of iron or other metal having a temperature coefficient of expansion considerably greater than that of quartz. The diameter of the wire is such that the joint remains vacuum-tight at the highest anticipated temperature, the joint being reinforced by cements which melt at such temperature. It is found that an iron wire of 0.5 mm. diameter affords a vacuum-tight joint in quartz-glass at a dull red heat, while wires of 0.9 mm. diameter may be heated to 360° C. without the joint leaking. In a lamp proposed by Belleaud and Barrollier [62] a heat conductor surrounds the electrodes so as to equalize the temperatures and prevent transference of mercury from the anode

[60] German Patent 336,570, May 11, 1920; J. Soc. Chem. Ind. 1921, *40*, 575-A.
[61] German Patent 336,014, September 24, 1918; J. Soc. Chem. Ind. 1921, *40*, 574-A.
[62] British Patent 168,022, December 10, 1920.

to the cathode. The heat conductor may consist of a gas under pressure or mercury in a sealed vessel surrounding the electrodes.

An arrangement by means of which the rays of a mercury vapor arc are obtained free from the effect of absorption is claimed by Kerschbaum.[63] In lightly loaded lamps the illuminating vapor uniformly fills the entire cross-section of the tube between the electrodes, but when there is an increased load and therefore higher temperature, the radiant vapor retreats from the walls of the surrounding tube, and forms an intensively radiant thread of light located in the axis of the tube, surrounded by comparatively weakly illuminating mercury vapor. The light of the bright radiant axial thread in order to be able to issue from the lamp must first penetrate the envelope of vapor and undergo absorption. To obviate this absorption effect the temperature of the envelope is reduced, and hence the concentration of the absorbing vapor is diminished. This can be effected by cooling outwardly, but owing to condensation of mercury vapor, a coating of mercury forms on the entire inside wall of the lamp and allows almost no light whatever to issue. To prevent condensation of the mercury vapor the arc is deflected toward one side of the tube of the lamp by means of an electromagnet, thus raising the temperature of the tube at the place where it is applied and burning for itself an aperture in the film resulting from condensation. The light of the deflected radiating arc will issue through this aperture without having penetrated an absorbing layer of mercury vapor. Figure 33 shows the form of construction of this apparatus.

The brass block (b) has a vertical bore; into this are soldered two tubes (r) having branches (w) for receiving and discharging the cooling water. Into this vertical cooler is inserted a quartz mercury vapor lamp (l), which is fastened above and below by means of bored rubber stoppers (d). The quartz lamp is a vertically burning lamp, which is of the simplest and most compact construction possible. As leading-in members for the lamp, ground-in nickel-steel pins (n) serve. Only the metal of the lower electrode (cathode) is mercury. The anode is a piece of carbon (c) screwed on the end of the upper nickel-steel pin. The brass block (b) has in addition, two lateral, horizontal, threaded bores. By means of these apertures the ends of two iron rods (m) are screwed up close to the wall of the lamp; over these rods are pushed coils of wire (e). Each of the two coils has 200 turns of covered copper wire of ½ ohm resistance; the current employed is 2-3 amperes. The electro magnets so formed produce lines of force at right angles to the axis of the lamp. The block (b) has another horizontal bore (f). This passes through only the rear half of the block and can be closed by a quartz plate. When the lamp is burning and the electro-magnets are so connected that they deflect the arc to the rear, the light will issue through the bore (f) and enclosing quartz plate. The arc is drawn by rotating the lamp into its horizontal position.

Buttolph,[64] tracing the development of mercury vapor lamps since 1901, points out that during the years 1902-07 the condensing chamber

[63] U. S. Patent 1,118,868, November 24, 1914.
[64] Gen. Elec. Rev. 1920, *23*, 741; 858.

was standardized, iron was adopted as the positive electrode material, and an automatic starting device was introduced; between 1907 and 1910 a commercial form of alternating current lamp was developed, and in the latter year a fluorescent reflector was put on the market; during the succeeding period a so-called orthochromatic lamp and a quartz mercury lamp were developed, and the problem of operating the alter-

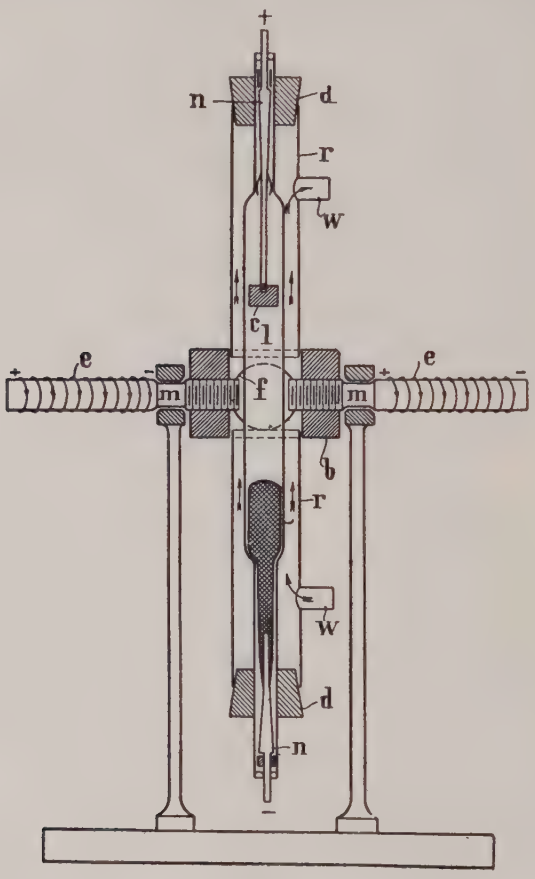


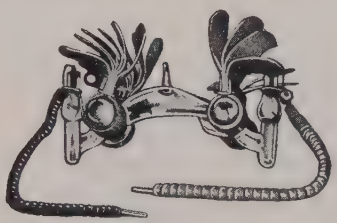
FIG. 33.—Kerschbaum's Apparatus for Magnetic Deflection of the Mercury Vapor Arc.

nating current lamp on a high power factor was solved. The two types of mercury vapor lamp have come into use: the glass tube with iron anode, and the fused quartz tube with tungsten anode, for low and high temperatures respectively. In the former the mercury cathode lies in a bulb-like condensing chamber; the latter has a mercury filled cathode chamber into which the arc is reflected by a bend of the tube. In manufacturing, the tubes are filled with twice the final amount of

mercury and heated almost to melting point of the tube. At the same time all gases are driven from the electrodes by operating them on 4000-6000 volts alternating current. The rapidly boiling mercury displaces all foreign gases, and the tube is sealed off.

Modern commercial mercury vapor lamps are of two main types; those having a mercury anode and those having an anode of tungsten or other metal. The first mentioned is built along the lines of the Heræus lamp and the electrical connections are made by means of ground-in pins of invar, an alloy possessing nearly the same coefficient of expansion as quartz.[65] The tungsten anode type is usually made with sealed-in connections, and a graded glass-to-quartz seal is employed to relieve the stress due to differences in expansion.[66]

Advantages are claimed by the manufacturers for both types of construction, but the difference is principally in mechanical features;



Courtesy Hanovia Chemical & Mfg. Co.

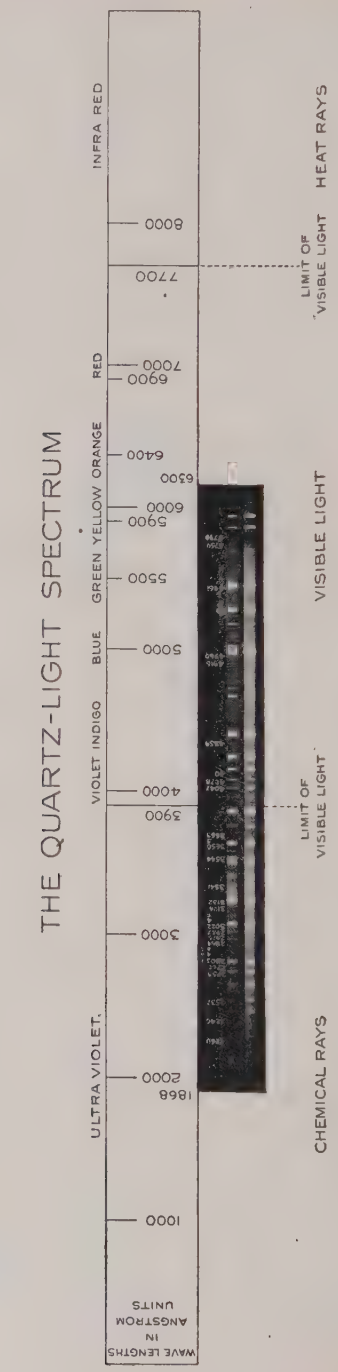
FIG. 34.—Hanovia Lamp for Direct Current.

the efficiency and spectral distribution of the light evolved being essentially the same.

For the mercury anode lamp with ground-in connections are claimed longer life and greater ease of repair. The tungsten anode lamps possess the advantages of greater facility in manufacture, mechanical simplicity, and ease of adaptation for operation in a vertical position.

The Hanovia quartz mercury arc lamp, see Fig. 34, consists essentially of three parts, the tube through which the arc plays, the anode vessel, and the cathode vessel. The current is carried to the lamp through nickel rods ground into the side tubes of the electrode vessels. The ground-in joints are sealed with mercury. Small quartz tubes are used in the electrode vessels to avoid "hammering" of the mercury. The lighting of the lamp is effected by turning the lever slowly around from position to position so that a stream of mercury flows from anode to cathode, making a short circuit between the two poles. On breaking the stream the arc is struck, and the lever must be brought back to its original position to allow the mercury to flow back into the anode vessel. After lighting, the lamp may be turned again by the lever into a vertical position in which it can be continuously used. The arc may be used end-on in a horizontal position by viewing it from the anode end, or in a vertical position from above. On 220-volt lines the lamp may be burned at all potentials between the electrodes from 25-185 volts by means of a variable resistance of 55 to 95 ohms (depending on the type of lamp) connected in series; on 110-volt lines at all potentials from 25-80 volts by means of a variable resistance of 25 or 40

[65] Hanovia Chemical and Manufacturing Co.
[66] Cooper-Hewitt Electric Co.



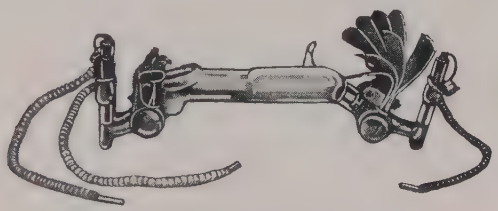
Courtesy Hanovia Chemical & Mfg. Co.

FIG. 35.

ohms. If the lamp is not required to burn at low voltages, resistances of 30 or 50 ohms and of 12 or 20 ohms suffice. At low potentials the arc or electric discharge fills the whole cross section of the tube. With increasing potential the cross section of the arc diminishes more and more, and forms eventually a thread of some five millimeters diameter. The specific intensity of the visible and ultraviolet radiation is the same, and the economy equally as good in 110-volt as in 220-volt lamps. With constant external conditions the light exhibits a desirable degree of constancy.

Figure 35 is a photograph of the spectrum of the Hanovia lamp, which gives an idea of the richness of the rays in the ultraviolet region; this is shown by the length of the spectrum falling to the left of line 3900 Å which portion of the spectrum is not visible to the eye. The Hanovia vapor lamp is also made for alternating current, the difference in construction being that for this current it is necessary that there be two positive electrodes in place of the one ordinarily used for direct current. (See Figure 36.)

A water-cooled lamp of the mercury anode type is in extensive use for medical work. (See Chap. 13.) The lamp consists of a U-shaped



Courtesy Hanovia Chemical & Mfg. Co.

FIG. 36.—Hanovia Lamp for Alternating Current.

tube, the bend of which is in a plane perpendicular to the plane of the arms. (See Figure 70.) The arc is formed in this portion of the tube which is surrounded by a jacket of quartz. Between this jacket and the outer housing of the apparatus water is circulated. The light is emitted through a quartz window in the front of the casing, after passing through the layer of water. The compact form made possible by this construction, known commercially as the Kromayer,[67] is advantageous for many purposes.

A form with a double anode for alternating current operation is also manufactured.

The "hot anode" type of quartz mercury vapor lamps, known as the "Uviarc," has no mercury chamber at the anode end.[68] In place of mercury, a tungsten target composed of a spiral formed of tungsten wire is used. The anode end is protected from mechanical injury by means of a metal cap which also serves to lead the current to the anode. The cathode end is reinforced with thick quartz to absorb the shock of the mercury vapor and is set at an angle which is claimed to reflect back into the luminous portion of the tube some ultraviolet rays which

[67] Hanovia Chemical and Manufacturing Co.
[68] Cooper Hewitt Electric Co.

would otherwise escape. The cathode end is also protected by a metal cap through which the current is led to the mercury. The tungsten wire, serving to lead the current into the lamp, is sealed into the quartz tube by a graduated mixture of quartz and glass so that at the end there is practically pure glass, while the portion next to the quartz tube is practically pure quartz. It is claimed that this combination of glass and quartz provides a proper coefficient of expansion so that the loss of vacuum is prevented. Having only one mercury electrode, this lamp is capable of being operated either in a vertical or horizontal position, which in certain cases is of advantage. (See Figure 37.)

A slightly different design is employed when tungsten anode ("Uviarc") lamps are intended to run generally in a vertical or nearly vertical position. The change is principally in the construction of the cathode chamber. (See Figure 38.) Double anode types for alternating current operation are also manufactured.

"Uviarc" lamps start with high current and low voltage when the tube is cold and the vapor pressure low. (See Figure 39.) For a given arc the starting current and the final arc voltage are determined by the

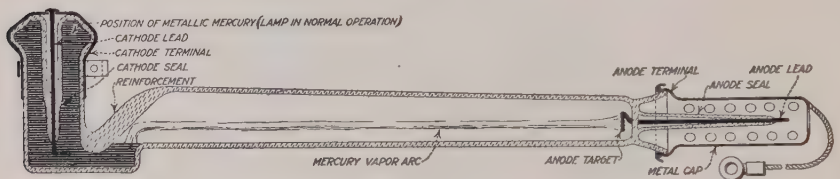


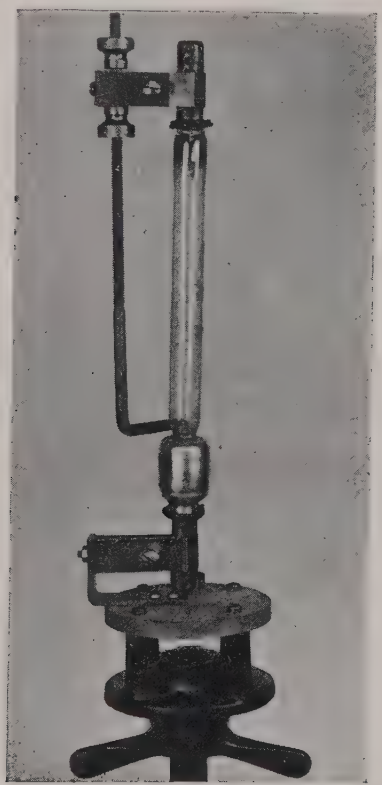
FIG. 37.

series resistance. Therefore a family of "starting curves" for different values of the series resistance is given in Figure 39; the locus of their terminations at operating equilibrium is the normal operating, or "stationary" characteristic, H-L, of this representative Uviarc. In the upper left hand corner of Figure 39, the volt and ampere components of the volt-ampere-time curve S-N have been separately plotted as functions of time and show clearly the way in which the arc comes to normal operation. As the temperature rises the vapor pressure and the voltage follow, while the current drops. Normal operation is reached when the heat radiated from the burner equals the electrical energy input and the vapor pressure no longer rises. This point is largely determined by the ventilation of the burner and by the room temperature. For example, with a given maximum burner voltage determined by the line voltage and the series resistance, the normal current is increased by cooling the burner. For this reason the 220-volt horizontal Uviarc requires about 4.5 amperes at 165 volts on the arc when operated in open air, while its normal current when enclosed is about 3.75 amperes at 174 volts on the arc. Thus temperature introduces another variable not represented in Figure 39.

During the transition from the low pressure arc starting condition to the high pressure arc there is a striking change in the appearance

of the luminous arc column. As seen through a dark filter the principal light source becomes concentrated in the center of the arc tube as a slender cord of great brilliancy. In this condition there is about 25 volts drop per inch in the arc as compared with approximately 1½ volts per inch in the low pressure arc.

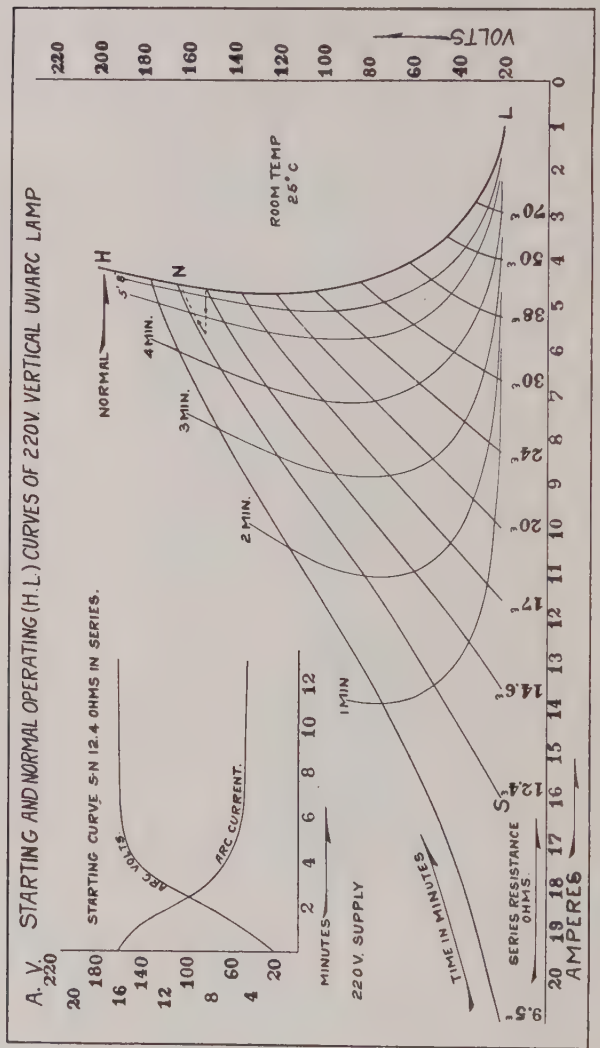
As indicated above, the Uviarc may be operated at various arc voltages from about 20 volts up to a certain maximum characteristic



Courtesy Cooper-Hewitt Electric Company.

FIG. 38.—Vertical Uviarc.

of each size of lamp. The curve expressing the relationship between the various arc voltages and the corresponding normal current is known as the "stationary" characteristic curve. (Figure 39, L-H.) The significant feature is the steepness of the curve for voltages above 80. There is a range of some 100 volts over which the current is nearly constant. This condition holds only for temperature equilibrium at the various operating wattages along the curve. The broken line shows approximately what happens when there is a sudden change in the line supply voltage to a Uviarc outfit. As apparent resistance of the arc changes



Courtesy Cooper-Hewitt Electric Company.

FIG. 39.—Starting and Stationary Operating Characteristic Curves.

only with the vapor pressure the first effect of an increase in the supply voltage is only an increase in the arc current. As in starting, with the resulting temperature increase, the burner voltage increases, the series resistance voltage decreases, the current decreases and normal operation is resumed at a higher burner voltage, but with practically the original current.

Buttolph [69] describes a small high intensity mercury vapor arc operating on 110 volts, either alternating or direct current. The effective light zone is ¼ x 1¾ inches, and is especially fitted for employment with suitable filters, as a monochromatic light source. By inserting resistance in series with the lamp, a low pressure arc giving only the strongest spectral lines is obtained.

The spectrum of the quartz mercury vapor lamp [70] extends from 185 to 1400 μμ (1850 to 14,000 Å). The radiation of wave-length less than 1400 μμ (14,000 Å) is largely concentrated in a close pair of yellow green lines at 576.4 and 579.1 μμ (5764 and 5791 Å), and a green line at 546.1 μμ (5461 Å). For this reason the visible portion of the spectrum is of unique value as a source of high-intensity monochromatic light for polariscopic, spectroscopic and interferometer work. The radiation of a wave-length less than 450 μμ (4500 Å) represents two-thirds of the total radiation of wave-length less than 1400 μμ. Like the visible radiation, the ultraviolet is concentrated in a few lines of high intensity. A pair of especially strong lines occurs at 365.0-365.4 μμ (3650-3654 Å), one at 398.4 μμ (3984 Å) and a pair at 404.6-407.8 μμ (4046-4078 Å).[71]

The results of an investigation by Coblentz, Long and Kahler [72] afford methods of determining quantitatively the decrease in intensity of emission with usage of quartz mercury vapor lamps. The measurements of the radiations from these lamps were made by means of a thermopile, in front of which was placed a 1 centimeter cell of water, to absorb the infra-red rays of long wave-lengths emitted by the electrodes. The variation in intensity of the ultraviolet rays was determined by observing the variation in transmission of a yellow Noviol glass, with usage of the lamp. It was found that the intensity of the total radiation, as well as the ultraviolet component, decreased to about one-half to one-third of its initial value in the course of 1000 to 1500 hours. During the first 500 hours' usage no marked difference was observed in the proportion of ultraviolet emitted by the two types of lamps tested. See page 256.

[69] J. Optical Soc. Am. 1922, *6*, 1066; also Chem. Abs. 1923, *17*, 653.

[70] Buttolph, Gen. Elec. Rev. 1920, *23*, 909.

[71] Of the various means employed to obtain the mercury spectrum, the best results were found by McLennan (Proc. Roy. Soc. 1912, A 87, 256) to be given by a Cooper-Hewitt glass lamp provided with a side-tube closed by a thin plate of crystalline quartz. The spectrum thus provided was observed to extend from 700 μμ to 215 μμ (7000 to 2150 Å). LeBlanc, Electrical Review and Western Electrician, 1910, 57, 1248, gives a description of construction of ultraviolet lamps, more particularly the Cooper-Hewitt lamp showing curves of current consumption and efficiency of the lamps.

[72] J. Frank. Inst. 1919, *187*, 112. Bur. of Standards, Sci. Paper 330, 1918. Note also Sci. Papers 378 and 495.

Courmont and Nogier[73] suggest that the diminution in the ultraviolet radiation from an old quartz mercury vapor arc lamp may be due to the fact that the inside surface of the quartz tube becomes gradually coated with a grayish deposit, or possibly that the gaseous composition in the lamp undergoes some change. The chief conclusion from these investigations is that, if it is desired to preserve a constant efficiency of ultraviolet radiation from the mercury vapor lamp, the temperature of the quartz must be kept low, perhaps by some cooling device. LeBon (Compt. rend. 1911, *153*, 49) also explains the deterioration of mercury vapor quartz lamps by the theory that the near surface of the quartz becomes covered with a thin opaque film. This film is formed with every kind of metal cathode and can be removed by rubbing with a cloth. Evans (Trans. Illum. Soc. 1913, 8) describes in detail various types of quartz lamps and gives curves and drawings illustrating the principal electric and photometric characteristics. The average life of the 220-volt type is stated to be between 2,500 and 3,000 hours before being re-exhausted. Lamps can be re-exhausted about three times.[74]

The total radiation of a quartz mercury lamp grows rapidly with increase of voltage and depends greatly on the degree of cooling of the lamp. The intensities of various portions of the spectrum do not grow with wattage at the same rate, and, on the whole, the infra-red and extreme ultraviolet grow the fastest. The radiation is affected by absorption by the luminous mercury vapor inside the lamp and therefore the dimensions of a lamp will affect its energy characteristics. The falling off in efficiency with age, due to devitrification and discoloration of the quartz, is most marked in the extreme ultraviolet.[75]

An ultraviolet radiometer devised by Anderson and Robinson[76] enables relative, and in some cases, absolute measurements to be made of the ultraviolet energy of quartz mercury vapor lamps. The following two stock solutions are employed. (1) Exactly 6.3 grams of pure tested oxalic acid crystals and 4.27 grams uranyl sulfate (UO_2SO_4-3 H_2O) dissolved in distilled water and diluted to exactly 1 liter. This solution must be kept in a brown bottle or in the dark. (2) An approximately 0.1 N solution of potassium permanganate to be standardized against the oxalic acid solution (about 3.16 grams per liter).

In order to make a relative determination of the amount of ultraviolet energy it is necessary only to expose to the radiation being measured exactly 25 c.c. of Solution (1) in a transparent, fused-quartz vessel. After a definite period of time, depending on the intensity of the light, the sample is removed and titrated against Solution (2). The result may then be stated in milligrams of oxalic acid decomposed or may be calculated to ergs. In making a relative determination it is, of

[73] Illuminating Engineer, London, 1911, *4*, 503.

[74] Boll (Compt. rend. 1913, *156*, 313; J. Chem. Soc. 1913, *104*, ii, 182) has made a study of the energy emitted by a mercury vapor lamp under varying conditions of voltage and current strength. The results show that the energy for 2536 Å emitted by the arc in mercury vapor is a parabolic function of the electrical power expended. This observation enables a formula to be derived by means of which an approximate calculation can be made for the radiation from such a lamp under any conditions. Allmand, J. Chem. Soc. Trans. 1915, *107*, i, 682, has considered the distribution of energy in the radiation from the Schott mercury Uviol-glass lamps.

[75] Reeve, J. Physical Chem. 1925, *29*, 39. See page 256.

[76] J. Am. Chem. Soc. 1925, *47*, 718.

course, necessary to maintain exactly similar conditions and to irradiate each time the same volume and area of solution. This method is readily adaptable to relative measurements of sources of ultraviolet radiation other than quartz mercury vapor arc lamps or as a method of comparison between the different sources.

An absolute measurement of ultraviolet radiation by this method is confined to the radiation from a quartz lamp, unless special care be taken. An absolute measurement of light is usually recorded in ergs per second per square centimeter. It is, therefore, necessary to note the area of surface of solution irradiated. A rectangular, fused-quartz cell is very convenient for this kind of determination. It should be so constructed as to permit a thickness of solution of 1.5 to 2 centimeters. The cell should be arranged so that the incident radiation may enter the solution through only one side. In measuring the distance between the light source and the cell, the center of the solution and not the wall of the cell must be taken as the point of measurement. In a nearly dustless atmosphere, the inverse-square law may be applied with accuracy over distances of 40 centimeters or less.

Athanasiu [77] finds the maximum sensitiveness of actinometers having electrodes of mercury salts in contact with 10 per cent sulfuric acid is at the following wave-lengths: mercurous chloride 2536 Å, mercurous bromide 2967 Å. The chloride and bromide are only sensitive to ultraviolet; they are fluorescent under its influence, emitting a strong visible radiation.

The potential gradient along the arc of a vapor lamp using the liquid alloy of sodium and potassium as terminals has been investigated by Newman.[78] This arc can be struck with 30 volts and when once started, the drop between the terminals being only 10 volts with a current of 1.5 amperes. The relative intensities of the potassium and sodium lines vary in different parts of the tube. The potassium lines are brightest near the anode, while at the cathode the subordinate lines of sodium are most intense. The cathode fall is greater than that of the anode, but both are small compared with results for other metal terminals. The potential drop along the arc column is uniform. The small potential drop between the terminals of the lamp when it is working is explained by the photoelectric effect exhibited by the alloy.

[77] Compt. rend. 1925, *180*, 587; J. Soc. Chem. Ind. 1922, 689-A; 1923, 686-A. An acetone-methylene-blue solution is used by Webster, Hill and Eidinow, Brit. J. Radiology, B.I.R. Section, 1924, *29*, 335. A solution of acetone in water is decomposed by ultraviolet rays, with formation of acetic and formic acids and other substances. The rays which have the most active biological effect are those with wave-length in the neighborhood of 3000 Å. Comparison of the bleaching of acetone-methylene-blue with the action on the human skin and on infusoria, for these wave-lengths, shows general agreement, both for solar and for artificial sources of radiation.

[78] Phil. Mag. 1924, *47*, 603; J. Chem. Soc. *126*, 222. In the vacuum mercury arc, Günther-Schulze, Z. physik, 1925, *31*, 509, finds that the cathode fall of potential is not very different from the ionization potential and about half the current is carried by electrons. Previous results obtained by using probe electrodes gave values much too low. At the anode, previous results obtained by calculation from the intensity of the radiation caused by the heating were much too high, as the energy of neutralization of the electrons had not been considered.

Metallic Vapor Arcs Other than the Mercury Type.

Heræus quartz lamps having electrodes of various metals and metalloids have been examined by Stark and Kuch.[79] The lamps are made in both of the forms indicated by Figures 40 and 41. Most of these are of little interest because of the difficulty of starting. The outer diameter is 0.9 centimeters, the length of the form shown in Figure 40 is 13 centimeters and of that shown in Figure 41 is 9 centimeters. Nickel rods serve to conduct the current to anode and cathode. The lamp is charged with metal by means of the container C shown in Figure 41. This is

FIG. 40.

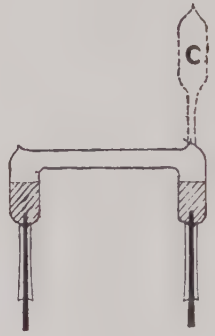


FIG. 41.

filled with molten metal and the tube evacuated when the metal passes into the lamp tube and the container C may then be removed by fusing the narrow part. The lamp is pumped out thoroughly while in operation in order to afford a satisfactory vacuum. To start the lamp a spark from an induction coil may be used, the metal being heated by a gas blast-lamp until sufficient metal vapors are produced to cause an arc to form. A voltage of 100-220 is used. The cadmium lamp is easy to start and operates at 2 to 5 amperes with metal cooling while with water cooling the lamp may be operated at 8 amperes. The zinc lamp is more difficult to start and requires heating with a blast lamp in order to put it into operation. With metal cooling the lamp will operate at 3 to 5 amperes. The lead lamp requires very intense heating in order to start. With water cooling it will operate at 8 to 10 amperes producing a strikingly rich spectrum. The bismuth lamp also requires intense heating when starting and with water cooling may be run at 7 amperes. The antimony lamp on the contrary is easily lighted and burns at 3 amperes, and it does not require water cooling unless a very strong current is employed. The spectrum covers a very wide range so that

[79] Phys. Zeitsch. 1905, *6*, 438.

bodies more nearly resemble their normal daylight color than when mercury or similar metallic arcs are employed. The antimony arc gives rise to very strong fluorescence effects. Sodium glass fluoresces strikingly with a greenish-yellow color, while lead glass exhibits a blue fluorescence. Tellurium and selenium lamps also have been tested. The former is operated at 6 amperes. The selenium lamp offers difficulties in starting.

An enclosed cadmium arc [80] proposed for polarimetric work consists of two electrodes of a silver-cadmium alloy, rotating in opposite directions on spindles driven from a small motor. On striking an arc between the electrodes, a brilliant spectrum is emitted, which includes the lines of silver and of cadmium. Although there is some flickering of the arc,

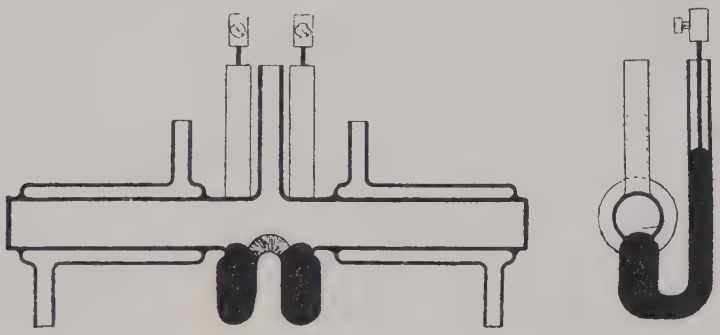


FIG. 42.—Cadmium Lamp.

this lamp can be used effectively if the polarimeter is provided with a constant-deviation spectroscope to purify the light before it enters the polarizer. But it cannot well be utilized with the simpler apparatus, in which the light is resolved only by a direct-vision prism on the eye-piece, as the unextinguished parts of the spectrum are usually too dazzling to permit of easy reading of any one line at the extinction-position. Another form of cadmium arc lamp, that of Lowry and Abram [81] shown in Figure 42, maintains the arc between water-cooled electrodes of solid cadmium; this is important, partly because it checks the vaporization of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped.

The lamp is operated in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and this must be pumped off in order to maintain the vacuum. Occasionally, when the vacuum is good, the arc will start itself by merely switching on the current, but usually it is necessary to start the arc by a spark. This can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In one form of the lamp these windows are protected from condensed metal by water-jacketing

[80] Phil. Mag., August, 1909.

[81] Trans. Faraday Soc., 10, 103. Note Bates, Phil. Mag. 1920, VI, *39*, 353. "Cadmium," Budgen, London, 1924.

the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube. The latter must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica is provided to bring the arc to the center of the tube. The cadmium arc will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of cadmium from the electrodes, which thus become shortened unduly.

Manufacture of Clear Fused Quartz.

For many years fused quartz has been made in small sections by hand labor in the ordinary blast flame using gas and oxygen. This has been accomplished by piecing together small fragments of quartz crystal in the flame, or by adding silica powder from time to time until the piece has grown to the heating limit of the flame. This obviously is a slow and expensive process. Developments by Berry [82] through a method of fusion in the electric furnace have made possible the production of fused quartz of the highest quality in large masses. The best grade of material is prepared from quartz crystals. It is much more difficult to make fused quartz of high quality from sand even though its purity may exceed 99 per cent. Therefore rock crystal is selected which is water clear and contains probably less than .2 per cent impurities. The surfaces often are encrusted with iron oxide and should first be washed in acids, then broken up and unsuitable pieces discarded. The most important step is the initial fusion. The clean quartz crystals or fragments of various sizes are packed as densely as possible in a graphite or carbon crucible. Cracking of the crystals is bound to occur as the temperature is raised and by packing densely the parts do not separate sufficiently to allow gas to penetrate crevices to any extent and thus form bubbles. The tightly-packed crucibles are placed in a vacuum furnace and the temperature is raised as quickly as possible to the melting point. During this initial fusion the pressure in the furnace is kept as low as possible. The time required for fusion of the charge will vary with the conditions but ordinarily about 45 minutes is required. The result of the initial fusion is a clear transparent mass containing comparatively few bubbles. These range in size from a pin point to 2 or 3 mm. in diameter. As these bubbles have been formed at a temperature of about 1800° C. the pressure at room temperature is very small. The mass is now ready for a second fusion to eliminate bubbles and obtain shaped products. The mass of material from the initial fusion is placed in another graphite crucible which is suspended in a vertical carbon tube furnace. A graphite piston which closely fits in the crucible is placed on top of the quartz mass and a weight is placed on the top of a plunger attached to the piston. The mass of quartz is again brought to fusion and due to the action of the weight the bubbles are largely collapsed. Thereupon the quartz is extruded in various

[82] Mr. Edward R. Berry, Assistant Director, Thomson Research Laboratory of the General Electric Company, assisted by Mr. L. B. Miller and Mr. P. K. Devers, conducted the research work which led to this achievement.

forms such as rods, tubes or ribbon. The material is practically free from bubbles but because of limiting dimensions it may become necessary to re-work. This may be accomplished by the usual bench methods with an oxygen-illuminating-gas flame. When it is desired to obtain large blocks as free from bubbles as the tubing, cane and ribbon, another operation is necessary. As before, the quartz is fused in a vacuum furnace which, however, is also designed to withstand very high pressures. As soon as the material is fused the vacuum valve is closed and the pressure in the tank is put under pressure. The pressure collapses the bubbles and makes it possible to obtain very large masses freer from bubbles than many kinds of the best optical glass. Not the least of the difficulties encountered in this development has been that in connection with the furnace equipment. The vacuum furnace in particular had to be greatly changed and enlarged. In addition to this the furnace had to be so constructed as to withstand repeatedly on the cover a total pressure of over 1,000,000 pounds (about 600 tons), and of course as the size of the furnace increases these difficulties are multiplied. Special attention must be paid to the design of resistor unit, to the thermal insulation and even heat distribution,—to the cooling of the terminals and many other factors presented in the use of these two extremes in pressure.

When the quartz crystal is heated between 500° and 600° it undergoes a remarkable physical change, cracking into small pieces, sometimes with explosive violence. This is due to the difference of coefficient of expansion along the two axes, subjecting the crystal thereby to great strain; and because of decrepitation owing to the presence of water and liquid carbon dioxide held in vast numbers of minute cavities throughout the crystal. The only advantage, therefore, in using large crystals for fusing lies in the greater ease of keeping the charge free from foreign material before the different particles begin to coalesce. Heraeus has heated crystal quartz in very small pieces, about the size of a nut, very slowly so that no cracking occurs and, consequently, no bubbles are included in the vitreous pieces. Herschkowitsch, on the other hand, has arrived at about the same result by accelerating the heating process so that a film of vitreous material is formed on the outside and prevents air from penetrating to the center, even though cracks may develop. As a matter of fact these processes, while interesting, are subject to very sensitive control and are impracticable where large masses are to be fused. To obtain masses quite free from bubbles, it has been found best to raise the temperature rapidly to 1400° or 1500° at which point the pieces begin to coalesce. At about 1750° C. the quartz is thoroughly fused though it is still very viscous. In fact, the viscosity is high even though the temperature be well over 2000° C. Vaporization of fused quartz is rapid at 1600° C. and at 1750° C. the loss due to evaporation is very great. Further increase in temperature results in no great gain in fluidity. By this process it is now possible to make tubes, rod, ribbon and cane in lengths of 30 feet and in shorter lengths of diameters up to eight inches. Blocks have been made up to 11½ inches in diameter and 6 inches thick having comparatively few

bubbles, and these widely separated, comparable in general appearance to the best quality of optical glass. Such material is suitable for prisms, lenses and for use in instruments where the invisible ray is an important factor. Fused quartz lenses 4½ inches in diameter have been for several months very successfully operated on test in motion picture projection machines, using currents as high as 150 amperes and under conditions where glass lenses cracked almost daily.[83]

[83] Berry and Devers (British Patent 222,119, Dec. 9, 1924) make silica tubing by feeding a quartz rod step by step from one end through a heating zone, where successive sections are heated to plasticity and expanded to tubular form by air or gas under pressure, supplied through a tube fused to the end of the rod. The heating is effected by a rotating ring of blowpipes. At the beginning of the operation the plastic end of the rod is perforated longitudinally by a forming tool to start the expansion. Molding devices are applied to the exterior of each section of the tube immediately after its passage through the heating zone. Other silica hollow-ware is similarly made from elongated pieces of quartz.

Chapter 4.

Protective Glasses and Filters.

In a volume on the chemical action of ultraviolet radiation, the inclusion of a chapter reviewing the subject of protective glasses may appear an unnecessary extension of the scope indicated by the general title. Mention of protective glasses is made here, however, mainly to remind the experimentalist not to disregard suitable protection for the eyes when working with these rays. Those desiring a more thorough knowledge of the topics of this chapter should consult the literature to which reference is made.

Exposure to rays emitted in electric welding and in the employment of the oxyacetylene torch for cutting and welding of steel has been the cause of many cases of inflammation of the eyes. The authors' attention has been called by experimenters working with the iron spark or arc to cases of painful eye irritation.

During the past few years the question of the injury of the eye by various industrial methods, especially those where intense heat or extremely glaring light is encountered, has borne much contention. There are on the market a host of glasses and goggles which are claimed by the manufacturers to have especial merits in protecting the eyes of workmen. In 1914 Crookes [1] investigated over 300 specimens of glass in the endeavor to find a colorless glass which would absorb all the ultraviolet and infra-red rays. Although he did not find a colorless glass which met this specification he developed a blue green glass which absorbed about 90% of the radiant heat.

The eyes require protection from intense light or glare, from ultraviolet radiation and from excess of heat rays. The ideal glass for goggles of general utility should combine absorptive qualities for each of these radiations.

We have, therefore, three divisions of radiation under consideration that are manifested respectively as infra-red or heat rays, visible light, and ultraviolet rays, the first and last being invisible. Andrews [2] affirms that ultraviolet rays are by far the most dangerous of all radiations to the eye, and the more so because they are not only invisible but also because we are unprovided by nature with any organ or sense for detecting them, so we know of them only by their effects. Fortunately the most deleterious of the ultraviolet rays, i.e., those rays having a wave-length of about 340 μμ (3400 Å) and less, are completely absorbed

[1] Trans. Royal Soc. 1914, *214*, *1*.
[2] General Electric Review, Nov. 1917, 9, 303.

by a moderate thickness of almost any ordinary kind of glass, so that, when their existence is known, their harmful effects on the eye can be easily guarded against.

The electric arc between carbon and iron, and iron and iron, according to Andrews, is one of the most prolific generators of these harmful rays, and operators on arc welding must necessarily be extremely careful in the employment of protective screens. Indeed, it may be stated that electric welding calls for eye-sight protection against intense heat rays, glare, flickering and ultraviolet rays. Notwithstanding this fact, however, complete immunity from bad effects to the eyes of operators can be assured by the proper use of protective lenses. The masks that are commonly used by operators not only are necessary for the protection of the face and neck from direct dangerous radiations but for the protection of the eyes from reflected ultraviolet rays; these rays together with heat rays can be reflected from a surface in the same way as visible light, so that complete protection can be assured only by cutting off all light from the eye excepting that which passes through the lens.

For the same reason arc welding should not be carried on in an open shop or even behind screens closed only at the sides. The reflection of the vivid and flickering flashes from the walls and ceiling may easily affect the eyes of other operators who are not engaged in welding, and are therefore unprovided with any protective device.

When mercury arc lamps are made of glass the emission of ultraviolet is largely arrested hence but little protection is required except from the glare. When made of clear quartz, however, they should never be used excepting when thoroughly screened by suitable glass shades, or eye trouble will ensue, since clear quartz is transparent to ultraviolet rays. Spectacles or eye glasses made with so-called pebble or crystal lenses (i.e., natural clear quartz) therefore afford no protection to the wearer; but the rays cannot pass as freely through the ordinary lenses of plain clear glass.

Only those who have experienced the baneful effects on the unshielded eye of the rays from an iron arc, such as is used in the cutting and welding of metals, can appreciate the acuteness of the pain resulting from such exposure. Aside from the inflammation, the eyes feel as if they had been rubbed with sandpaper or as some have expressed it, "full of sand" due to the roughening action by the rays on the delicate membranes.

In arc welding, using 100 volts or over, the rays are very destructive and may penetrate clothing, causing blistering of the skin. Workmen's ordinary cotton gloves should not be worn, thick, heavy gloves being required. The abdomen should be well protected by heavy clothing. At 30 volts or less such precautions are not as urgent. The eyes, however, irrespective of the voltage, should be carefully shielded. A simple device is a spectacle frame provided with a rectangular support for colored glasses. A red and a blue glass with or without a piece of uncolored glass on the exterior side protects well from glare and destructive rays. Some operators, however, prefer a higher degree of visibility so as to better distinguish molten iron from slag. In this case one may use a

sheet of ruby red glass together with an emerald green glass, preferably also with a sheet of uncolored glass on the outer side of the frame. Such protectors are inexpensive and have been used to a considerable extent in this country by arc welders.[3]

Large commercial electric furnace units employing many thousand amperes emit rays of a particularly vicious nature during the melting down period. The rays are hurtful even at long range, and so far as the eyes are concerned, by exposures scarcely more than momentary, or lasting only one or two seconds. The utmost care should be observed to protect the eyes when in the neighborhood of furnaces of this character not adequately closed during the melting down period. At a later stage, when the atmosphere of the furnace is heavily charged with vapors of calcium, the absorption of ultraviolet in this atmosphere is so great that the danger of injury is greatly diminished.

Kindall[3a] reports that of thirty men who were viewing the demonstration of a portable electric arc welding outfit, seventeen reported to a physician for treatment a few hours later, suffering from traumatic conjunctivitis. In two cases the pain was very severe and the symptoms were similar to those of irritis. Morphine had to be administered to afford relief from the pain. Only two of the thirty men were not affected in some way from this exposure, these two wearing thick-lensed orange-colored glasses. Several of the men wore orange-colored glasses with thin lenses, but the latter were not heavy enough to afford protection against an exposure as long as took place. Conjunctivitis is an inflammation of the conjunctiva, the mucous membrane covering the inside of the eyelids and part of the eyeball. Traumatic conjunctivitis is caused by foreign bodies in the eye, exposure of the eyes to high winds, dust, smoke, intense light from electric arc lamps and from electric-welding apparatus. In the instance mentioned above, the inflammation was due to the ultraviolet rays. In some cases the effect is so severe that, in addition of conjunctivitis, an inflammation of the skin similar to sunburn is produced. The symptoms of conjunctivitis caused by intense light or by the ultraviolet rays are abnormal intolerance to light, excessive secretion of tears, intense smarting of the lid, contraction of the pupil, sometimes swelling of the lid and small ulcers developing on the eyeball or cornea. Unless properly treated by a physician immediately, chronic inflammation of the conjunctiva, cornea, iris, or retina, and possibly blindness, may result. Under proper treatment most cases recover in a few days. When electric arc-welding is being carried on glasses should be worn, the lenses of which are made up of alternate layers of red and blue glass or orange glass of sufficient thickness to protect the eyes from the effects of ultraviolet rays.

Steinmetz observes that blood is practically opaque to the rays and on exposure of the body thereto, the rays penetrate but slightly beneath the surface where they are absorbed by the blood. He also observes that complete recovery from ultraviolet burns may be extremely slow, taking months or even years for practically complete recovery and in some cases where the burn has been unusually severe some after effects, such as, for example, abnormal sensitivity to radiations of short wave-length, may be practically permanent.[4]

[3] Irritation of the eyes caused in this manner may be ameliorated by the following eye lotion, with which the eyes may be bathed as often as required. Boric Acid, 60 grains; Laurel Water, ½ ounce; Rose Water, 8 ounces. The lotion is somewhat more soothing than a simple aqueous solution of boric acid.

[3a] Chem. & Met. Eng. 1920, *23*, 1071.

[4] Radiation, Light and Illumination.

The lens of the eye protects the retina from the influence of ultraviolet rays. When strongly irradiated by ultraviolet the lens becomes fluorescent and the ultraviolet has, therefore, been converted into visible light. This raises the question whether the energy continually striking the eye may not, in time, effect appreciable alterations in the organ. Widmark, Schuleck and other workers have detected a cloudy formation in the lens under the influence of ultraviolet rays. The efficiency with which the eye is protected from ultraviolet is discussed by Bell,[5] who states that under ordinary conditions tests have shown that no permanent effect is caused by exposing the eye to ultraviolet rays. In cases where the exposure is severe, lenses should be provided, but the choice of glass is a matter of taste, ordinary optical glass being almost opaque to ultraviolet rays. Of the colored glasses, ordinary commercial amber glass seems to be as effective as special glasses. Although, in the lightest tints, traces of ultraviolet will pass, if the color is deep enough to cut down materially the visible light these traces will disappear. It will be noted that the conclusions of Bell are not entirely in agreement with those of numerous other observers, some of whom appear to be warm advocates of certain proprietary glasses.

According to some authorities the production of cataract may be at least partially due to the action of rays of short wave-length which have been proven to give rise to a certain turbidity of the eye lens, when present in large quantities. In particular it has been suggested that the prevalence of cataract among glass workers might be explained in this way. Schanz and Stockhausen have declared that ordinary glasses, and even those constructed of blue glass, fail to stop the ultraviolet rays of the most dangerous nature.[6]

While developing certain blue glasses Luckiesh[7] noticed that cobalt glass appeared to be more transparent than clear glass to ultraviolet rays in the neighborhood of 300 μμ (3000 Å). Conclusive evidence was obtained by means of clear and blue glasses (soda-lead) of (1) equal thickness and (2) of the same content except that the blue glass contained in addition a very small percentage of cobalt. Clear and blue specimens of the same thickness were compared in pairs by photographing the spectrum of the quartz mercury arc through each. These experiments established the fact that the glass containing the slight amount of cobalt was more transparent to the mercury lines near 300 μμ (3000 Å). Since this observation was first made it has appeared to Luckiesh that certain blue glasses which have been developed chiefly for scientific purposes owed a portion of their usefulness to this augmented transparency in the region of 300 μμ (3000 Å).

[5] American Academy of Arts and Sciences, 1911, 671.

[6] They suggest the desirability of using a special "euphos" glass which is completely opaque to the objectionable radiation. Illuminating Engineer, London, 1908, *1*, 820. Inagaki reports that "Noviweld" and certain Crookes glasses are suitable for specified uses in glass plants. Rept. Lab. Asahi Glass Co. 1921; Chem. Abs. 1922, *16*, 3185.

[7] J. Franklin Inst. 1918, *186*, 111.

Glasses are described by Coblentz and Emerson [8] for protecting the eyes from injurious radiations. Against ultraviolet rays—black, amber, green, greenish yellow and red glasses are efficient. Spectacles made of white glass afford some protection from the extreme ultraviolet rays which come from quartz mercury vapor lamps and from electric arcs between iron, copper or carbon. The vapors from these arcs emit but little infra-red radiation in comparison with the amount emitted in the visible and in the ultraviolet. For shielding the eye from infra-red rays, deep black, yellowish green, sage green and gold-plated glasses, are efficient. For working near furnaces of molten iron or glass, if considerable light is needed, a light bluish green or sage green glass is efficient in obstructing the infra-red rays. For working molten quartz, operating oxyacetylene or electric welding apparatus, or other intense sources of light, it is important to wear the darkest glasses one can use, whether black, green (excluding gold-plated glasses), or yellowish green, in order to obstruct not only the infra-red but also the visible and the ultraviolet rays.

Gibson and McNicholas [9] have investigated many of the extensively advertised glasses on the market for the protection of the eye and have measured the absorption of light by these glasses for definite given thickness. Coblentz [10] concludes after his investigation of various commercial protective glasses that red glass absorbs the ultraviolet, most of the visible rays and practically no more of the infra-red than clear glass. Amber glass absorbs the ultraviolet and some of the visible spectrum. Green glass is opaque to ultraviolet and has a wide absorption at about 1 μ. Blue glass transmits ultraviolet, but absorbs in the visible spectrum. Sage green or blue green absorb the ultraviolet and infra-red. Black glass does not give sufficient protection if working near a source of intense ultraviolet, but absorbs strongly in the visible spectrum. A thin film of gold absorbs the infra-red and ultraviolet and to some extent the visible rays depending largely upon the density of the film. "Noviweld" absorbs effectively the ultraviolet and infra-red rays. Dyes as a rule are not satisfactory due to the difficulty in securing one which is sufficiently stable and which has the proper absorbing powers to afford complete protection.

Crookes [11] succeeded in preparing glasses which cut off more than 90% of the heat radiation, which are opaque to the invisible ultraviolet rays, and are sufficiently free from color to be scarcely noticeable when used as spectacles. It has not been possible, however, to combine in one specimen of glass these three desiderata in the highest degree. The ideal glass which will transmit all the colors of the spectrum, cutting off the invisible rays at each end, has still to be discovered.

A glass for absorbing ultraviolet radiations advocated by the Corn-

[8] U. S. Bureau of Standards Techn. Paper No. 93, 1917; J. Frank. Inst. 1917, *183*, 629.
[9] Jour. Franklin Institute, 1919, *187*, 630.
[10] *Ibid.*, *188*, 255.
[11] Phil. Trans. 1914 (A), *214*, 1.

ing Glass Works [12] is made by adding to an ordinary lime, barium, lead, or zinc glass batch; (A) at least 6 per cent of titanium dioxide, and oxidizing salt (nitre) in sufficient quantity to prevent the reduction of the titanium dioxide, with or without cerium oxide or vanadium oxide; or (B) at least 1 per cent of a higher oxide of vanadium than V_2O_3, with or without an oxidizing agent (nitre) and a complementary, but absorptively inert substance (manganese dioxide, cobalt, nickel or uranium oxides) to change the hue of the glass from green to amber. Titanium dioxide is about half as effective as cerium oxide. A lime-soda glass containing 7.7 per cent titanium dioxide and 7.7 per cent cerium nitrate is brilliantly clear yellow, and in plates two millimeters thick completely cuts off the 0.365 ultraviolet line. A glass containing both cerium nitrate and titanium dioxide has a more brilliant color and greater desirable absorption than a glass containing one of these substances superimposed on a glass containing the other. The addition of borax to the glass batch increases the refractive index of the glasses containing titanium dioxide. Reduction of higher vanadium oxides to V_2O_3 must be prevented, as the latter does not cut off the ultraviolet rays. A large proportion of borax in the glass containing vanadium oxide completely cuts off the ultraviolet 0.365 line in plates of 4 millimeters thickness, and if 2 per cent of vanadium oxide be used the same cut-off is effected in plates 2 millimeters thick.[13]

The absorption of ultraviolet by various kinds of glass was investigated by Ham, Fehr and Bitner [14] for the purpose of finding suitable protective glasses for the eyes. It is concluded that glass is opaque to wave-lengths below 302 μμ (3020 Å) and therefore the rays which are generally conceded to be extremely harmful are cut out. Until more data are obtained it is recommended that those glasses which do not absorb almost completely at 365 μμ (3650 Å) should be rejected.[15]

[12] British Patents 118,397 and 118,398, April 15, 1918; J. S. C. I. 1918, 584 A.

[13] Taylor, U. S. Patents 1,292,147 and 1,292,148, states that glass for absorbing ultraviolet rays is formed with titanium oxide as an essential constituent. The glass batch may be made up of sand 49-60, soda 21.75-25, nitre 4.6-5.2, calcium carbonate 0-6, titanium oxide 4.25-8, cerium nitrate 0-7.7, vanadium oxide 0-0.35, borax 0.67-1 and arsenic 0.4-0.5 parts. A clear, brilliant yellow or yellow-green glass is produced suitable for optical uses. Taylor, U. S. Patent 1,414,715, May 2, 1922, obtains a flesh colored glass of high ultraviolet absorption and good visible transmission by using 3-6 per cent cerium dioxide and 0.2 per cent manganese dioxide with silica, potash, soda and lime. Less than 1 per cent of the rays of wave-lengths under 3550 Å are transmitted by a glass of the composition SiO_2, 70 per cent; K_2O, 8 per cent; NaO, 11.8 per cent; CaO, 5.5 per cent; CeO_2, 4.5 per cent; MnO_2, 0.2 per cent.

[14] Penn. State College Report, 1914, Part 1, 158, published 1916.

[15] Voege, Illuminating Engineer, London, 1909, *2*, 543, has made a thorough investigation of the relative efficiency of various types of glass and in varying thicknesses. Photographs of spectra of the Heræus quartz lamp taken through these glasses of varying thickness are given and recommendations of types of glass suitable for special glass are made. Zschimmer, Chem. Central-Blatt, 1903, *74* (2), 1360, studied the transparency of various types of glass to ultraviolet rays. Several types of glass are described together with the wave-lengths to which they are transparent. Schjerning, Ann. der Physik und Chemie 1887, 11, 340, made the observation that optical glass absorbed ultraviolet and made measurements of several glasses of different densities in regard to their absorp-

Filters: While the subject of protective glasses considers mainly the exclusion of ultraviolet rays, the investigator has to call frequently on means which exclude visible rays or which serve to extinguish some part of visible or invisible radiation. Many types of screens or filters have been proposed, some of which find mention in the following data. The most interesting are those directed to accomplish the exclusion of visible rays since thereby not only are effects astonishing to the layman obtainable but also photographic methods applied to various physical phenomena lead to discoveries of importance. In order to accomplish this exclusion suitable screens must be employed in conjunction with the present sources of ultraviolet rays. Lenses of quartz, coated with silver, cut off the visible rays but transmit ultraviolet. Wood [16] observes that dense cobalt-blue cells filled with a solution of potassium bichromate make possible photographs in infra-red rays. These rays are not scattered by the atmosphere, while ultraviolet rays are so scattered that it is unlikely that any of them reach us from the sun; such rays as do reach the earth coming from the sky. Uranium nitrate shines when exposed to ultraviolet rays, while vapors of mercury may be seen rising from a body of mercury even at room temperature when photographed in ultraviolet.

A number of physical changes of a striking character are obtainable by means of an ultraviolet lamp, well screened to prevent the passage of visible light. Fluorescent effects in great variety are easily secured. In a darkened room irradiated only by ultraviolet, the teeth, eyes and even the fingernails glow with a weird yellowish fluorescence; a transformation always amusing to the observer who witnesses this phenomenon for the first time. Artificial teeth do not become fluorescent but appear black, hence the oral cavity may present a grotesque cast, often rendering one's neighbor scarcely recognizable.

Michaud and Tristan [17] describe a method of making an ultraviolet lens which will exclude all light other than the ultraviolet. The lens

tion. Schönn, Ann. der Physik und Chemie 1880, *10,* 143, has examined the transmission of ultraviolet rays through various substances such as glass, gypsum, alum, sugar, etc. A series of soda-lime glasses of similar composition, one free from coloring agent, some colored brown by selenium and some blue by cobalt oxide, were exposed by Clarke, J. Soc. Glass Tech. 1921, *5,* 155, to the action of ultraviolet rays. None of the glasses was colored by the rays, but a slight amount of fluorescence occurred in the case of the pure soda-lime glass and the selenium glass. Voege, Elektrotechnische Zeit. 1908, *29,* 779, discusses the use of various types of globes for the protection of the eye against the harmful effects of light. Helmets of fiber have been constructed finished within and without in dead black so as to minimize the danger from reflected light. The top of the head is protected by a fireproof cap, to which the helmet is pivoted so that it may be turned back out of the range of vision when it becomes necessary for the wearer to inspect his work or to move about. The lenses mounted in this helmet are a combination of "Ark-weld" and "Akopos" glass, the former to reduce the intensity and the latter to eliminate the injurious rays of the arc light. According to Bellile, Illuminating Engineer, London, 1909, *2,* 490, it is necessary to protect the eyes of wireless telegraph operators from the effects of the spark by enclosing the latter in an envelope opaque to ultraviolet rays.

[16] Smithsonian Institute 1911, 155.

[17] Scientific Amer. 1912, *107,* 257.

proper is composed of quartz and is coated with a layer of silver which is precipitated on the lens from an alkaline silver solution by means of a 10 per cent solution of milk sugar. It is claimed that this covering is much superior to silver leaf coating. A number of flowers photographed with this lens,[18] whether white or colored, left a black or dark gray image on the photographic plate while in visible light they came out in widely different shades. Another group of flowers, to which Michaud and Tristan gave the name of ultraviolet flowers, and mostly yellow in color, were reproduced by ultraviolet much as in ordinary light.

In order to prepare a ray filter which will allow only the waves of a definite length to pass, Peskov [19] states that it is necessary to calculate the coefficient of absorption of the substance and then determine the density and thickness of the solution so that the desired quantity of waves of a definite length will pass the filter. With visible light this separation is an easy matter, for there are various measuring instruments such as the spectrometer which give a direct reading, but in the invisible portion of the spectrum the separation of the wave-lengths from each other in a definite manner is quite difficult. Dyes are not suitable for use in some filters as they show more or less distinct absorption bands in the region of the shortest ultraviolet. Chlorine is the best suited for this purpose since the maximum absorption is in the region 380-300 μμ (3800-3000 Å). Bromine gas cuts out the visible part of the spectrum entirely up to 380 μμ (3800 Å) and its absorption capacity ends slightly beyond the point when chlorine absorption begins. In water solutions the absorption phenomena of these two gases changes, which Peskov attributes to the formation of complex molecules of halogen and water.

Silver, either in the form of plates or in the colloidal state, was not satisfactory as the absorbing capacity ends at about 400 μμ (4000 Å) and on increasing the concentration, absorption in the short ultraviolet region was noted. Uviol glass is a species of glass especially permeable to ultraviolet rays although it does not permit the passage of the extremely short waves.[20] Uviol glass permits ultraviolet rays of a wave-length to 253 μμ (2530 Å) to pass.

A discussion of ultraviolet ray filters by Miethe and Stengel [21] gives a list of various dyes which are suitable for this purpose together with the range of wave-lengths which will be effected by given concentrations of the dye. It is the opinion of Potapenko [22] that the most suit-

[18] Scientific Amer. 1914, *111*, 301.

[19] J. Phys. Chem. 1917, 382.

[20] Weyl, Die Methoden der Organischen Chemie, Leipzig, 1909, *1*, 312. Henri, Compt. rend. 1922, *155*, 315, made a study of ultraviolet rays below 300 μμ (3000 Å) using screens to arrest certain portions of the ultraviolet spectrum. Determinations of the amount of energy transmitted by viscose, glass, cellulose acetate, a solution of acetone, and by egg-white as a type of protoplasm, show that the effect of the ultraviolet rays increases continuously as the wave-length diminishes, and that it is proportional to the coefficient of absorption by protoplasm. Dussand, Compt. rend. 1899, *128*, 174, has made observations on the transmission of ultraviolet rays by means of a series of lenses and prisms.

[21] Z. wiss. Phot. 1919, 19, 57; J. S. C. I. 1920, 39, 313 A.

[22] *Ibid.*, 18, 238; Chem. Abs. 1920, 699.

able form of light-filter for Uviol lamps is a stained gelatine film, which may be prepared by coating glass with a gelatine solution containing the dye, and after drying, stripping the film so formed.

Wood [23] has suggested the use of nitrosodimethylaniline in order to construct screens that should be transparent only to ultraviolet rays. Its peculiar optical properties render this compound of utility. Plotnikow [24] has described a variety of filters suitable for use with a mercury vapor lamp for the purpose of isolating definite regions in the spectrum. The coefficient of absorption, in a number of gases, of light after passage through quartz windows has been measured by Varley.[25] Another light filter for ultraviolet rays is described by Mannich,[26] a substance which absorbs light waves of a given length being used. Cinchonine sulfate, triphenylmethane, etc., are suggested. The use of quartz glass, uviol glass and euphos glass is also discussed. Lehmann [27] states that when preparing a filter for cutting off a certain wave-length it is advisable at times to add some other substance which would also cut off the heat rays. The separation of visible from ultraviolet rays may be carried out by means of a solution of quinine sulfate which is colorless and permits visible light to pass through readily while it is opaque to ultraviolet rays shorter than 400 μμ (4000 Å).[28] Clark [29] describes a light filter for absorbing blue-violet and ultraviolet rays. It is formed of gelatin or other light-transmitting material containing a salt of glucosephenylosazone p,p′-dicarboxylic acid. A filter for ultraviolet rays used by Lehmann [30] consists of a vessel of Jena blue Uviol glass filled with copper sulfate solution, and coated on the outside with a preparation of nitrosodimethylaniline and gelatine. A quartz lamp or an iron arc is used as the source of ultraviolet rays and lenses of quartz or special crown glass for concentrating the rays. In describing the possible applications of such a light filter, it is pointed out that on exposure to the rays, chemically pure substances exhibit luminescence only faintly, whereas commercial products of second quality show a very strong luminescence. Different types of glass each exhibit characteristic fluorescence-colors. Many substances exhibit notable phosphorescence; rods of fused sodium hydroxide, for example, show a reddish white effect in the cone of ultraviolet rays, and a green color when rapidly moved away.

Figure 43 shows the relative transmission of quartz, certain glasses and filters for various wave lengths, and also the distribution of energy in the mercury vapor arc.

For the isolation of the various mercury lines two general methods are available. For ordinary polariscopic and general laboratory work, as noted, filters will be found satisfactory. For exact physical measure-

[23] Phil. Mag. 1903, 257.
[24] Photochemische Versuchstecknik, Leipzig, 1912.
[25] Proc. Camb. Phil. Soc. 1904, 510.
[26] Chem. Zeit. 1909, *33*, 1167.
[27] Chemiker Zeitung 1910, *34*, 1032.
[28] Weyl, Die Methoden der Organischen Chemie 1909, Vol. 1, 313.
[29] U. S. Patent 1,293,039, Feb. 4, 1919.
[30] Physik. Zeits. 1910, 1039: Chem. Zent. 1911, *1*, 55.

TABLE 1

Radiation	Corning Glass	Eastman Wratten	Liquid Filters
Infra red or 10,140	G554EK, 6-8 mm	88 as used by R. W. Wood or 89A	Cobalt Blue Glass and Saturated Solution of Potassium Dichromate
5769-90	G34R, 3-4 mm	22, Hg. Yellow	Chrysoidine and Eosine
5461	G555Q, 8-10 mm and G34Y, 3-4 mm	62 Hg. Green or 77 Hg. Special or 77 A. Hg. Special for Interferometry	Neodymium Ammonium Nitrate and Potassium Dichromate
4359	Noviol A, 3.0 mm and G585, 3-5 mm	50 Hg. Blue	Cobalt Blue Glass and Quinine Sulfate
4047-78	G586A, 3-5 mm and Novoil 0, 3-4 mm	36, Hg. Violet	Methyl Violet and Quinine Sulfate
3650 3656 3663	G586AW, 8-10 mm	18, Ultra-violet	Methyl Violet and Acid Green
To absorb Infra red	G392, 6-10 mm	.....	Cupric Chloride 2% Solution
Fluorescence	G371R, 2-3 mm	.....	Fluorescein or Rhodamine B

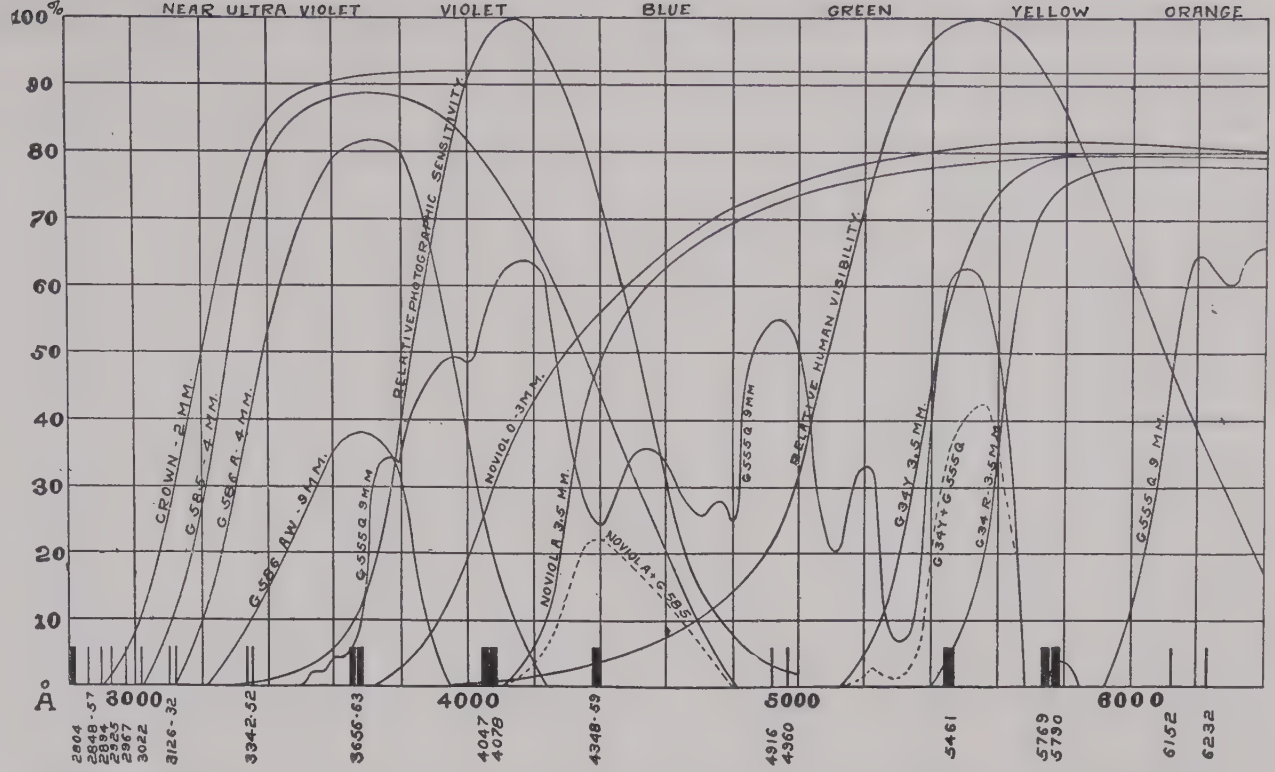
Courtesy Cooper-Hewitt Electric Company.

ments, however, an optical method of spectrum line isolation is necessary.[31]

Three types of filters are available as listed in Table I. Gelatine and liquid filters must be kept as nearly as possible at room temperature. Table 1 and Figure 43 show a number of filters and their transmissions. The liquid filters, all of which are two cell combinations, are best adjusted for the desired effect at the time of use. Wratten gelatine filters [32] are satisfactory for many purposes because of the large number

[31] See Bur. of Standards Circ. 44, 1918; Bull. 534, 1906. As Mathews, Ind. Eng. Chem. 1923, 887, rightly observes, photochemical reactions usually are sensitive to a comparatively narrow band in the spectrum. If a wide band is used, energy is therefore wasted, and an undesirable result may be produced. Now that light is playing an increasingly important role in the photosynthesis of many compounds, it becomes more important that sources of very intense monochromatic illumination be developed. The present practice is either to secure approximately monochromatic light by dispersion of light through a prism, letting the desired wave-length fall upon a slit behind which the reacting system is placed, or by the use of filters designed to filter out the wave-lengths not desired. In either case, the intensity of the resulting illuminating beam is not great, particularly if it is anywhere near monochromatic. In order that reactions may be carried out on anything like a commercial scale, better means of producing powerful, intense sources of such light must be developed. Note Coblentz and Kahler, Bur. of Standards, Sci. Paper 378, April 9, 1920.

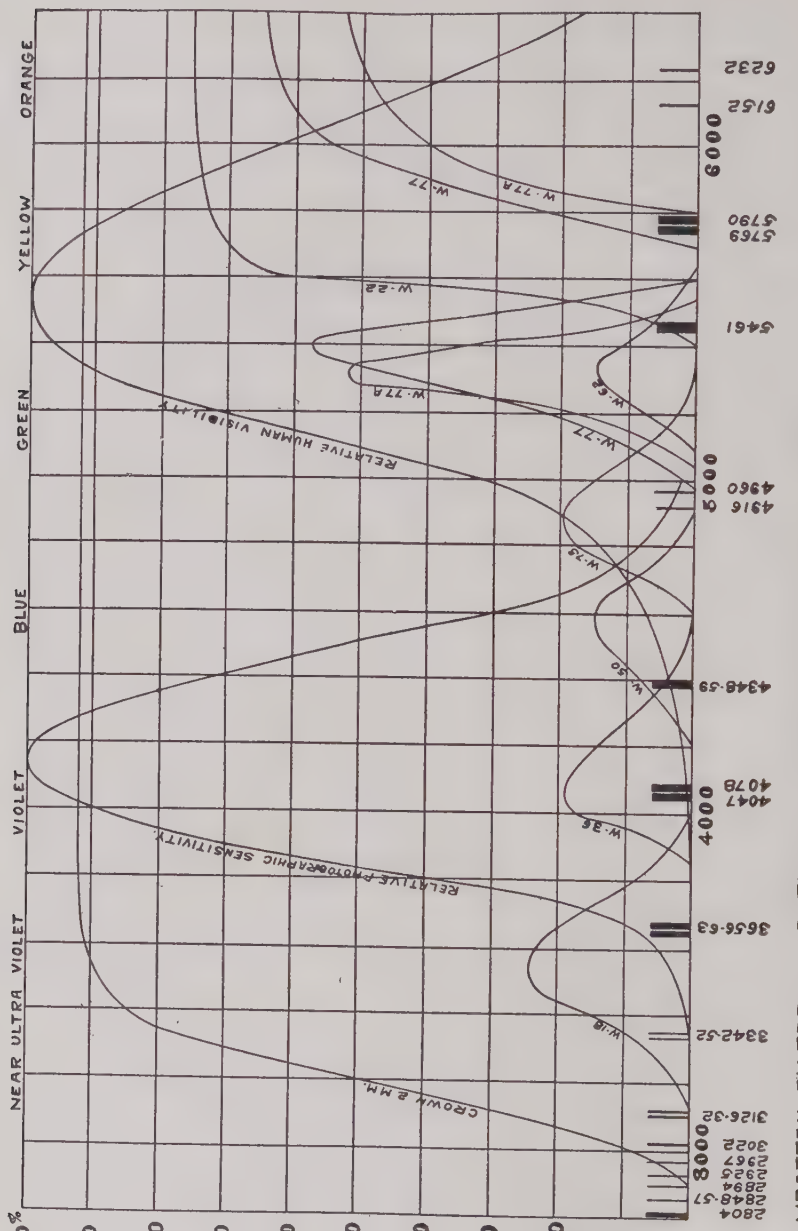
[32] Eastman Kodak Co. "Wratten Light Filters" 1922.



CORNING FILTERS - DATA FROM CORNING GLASS WORKS AND BUREAU OF STANDARDS.

Courtesy Cooper-Hewitt Electric Company.

FIG. 43.



WRATTEN FILTERS DATA FROM EASTMAN KODAK COMPANY.

Courtesy Cooper-Hewitt Electric Company.

FIG. 44.

that have been closely standardized. There are available a number of filters known as "Mercury Monochromats" whose transmissions are shown in Figure 44.

Corning glass filters [33] are most satisfactory where their thickness and consequent bulk are not objectionable, and where appreciable heat must be dealt with. As is apparent from Figure 43 they generally have rather broad but high transmission characteristics and hence are used in combination to secure the desired effects.

Andrews [34] furnishes details of an apparatus for separating visible from invisible light, the theory of the apparatus being that the visible light is less refracted by a lens than is ultraviolet radiation.

Figure 45 diagrammatically shows the design of the apparatus. *A* is a source of visible light, also producing ultraviolet rays, such as may be produced by a high tension disruptive spark between iron terminals. *B* is a quartz lens. *D* is a thin sheet of metal pierced with a pin-hole at *C*, the diaphragm being so placed that the pin-hole is in the exact mean focus of the ultraviolet rays. *E*

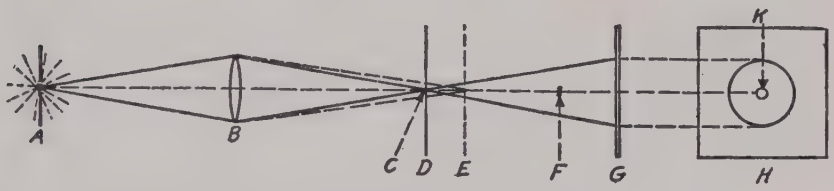


FIG. 45.—Diagram Showing Principle of Andrew's Separator.

indicates the mean focus of the visible rays. *F* is a small metal disk and *G* is a screen. A front view of the screen is shown at *H*. The operation of this instrument is based on the fact that the mean focus of visible light is located at a measurable distance beyond the mean focus of the invisible rays owing to the greater refrangibility of the latter over that of the former. If, therefore, the diaphragm *D* is carefully adjusted so as to bring the pin-hole *C* into the exact mean focus of the ultraviolet rays, the rays of the latter will pass through the pin-hole and spread out again on the other side of the diaphragm. The mean focus of visible light being some distance beyond the pin-hole, its rays will be largely intercepted by the diaphragm, and through the pin-hole only a few of the nearly parallel rays of visible light will pass. In operation, if the screen *H* is made of non-fluorescent material, there will appear on it only the small illuminated spot *K*, but if it is coated with a fluorescent substance, such as powdered willemite, this small luminous spot will be surrounded by a disk of bright green light produced by the fluorescence of the willemite excited by the circular field of invisible ultraviolet rays. Should it be found desirable to cut out the spot of visible light, the small metal disk *F* can be set up in such a position as to cast its shadow over the spot *K* and so transform it from a bright spot to a dark one, leaving the disk of green fluorescent light otherwise unchanged.

This apparatus is valuable for the determination of the exact fluorescent colors of various compounds. When such compounds are exposed to the direct rays of an open iron spark, their true fluorescent color is

[33] Bureau of Standards Technologic Paper 119, 1919; 148, 1920; Scientific Paper 325, 1918.

[34] General Electric Review, 1917, 817.

masked to a greater or lesser degree by the visible light component of the spark, this being especially the case with compounds that show only a weak fluorescence. When a compound is placed within the invisible field of the ultraviolet rays of this separator, it shows its true fluorescent color and the fluorescence, if pronounced, manifests itself on a visually dark field, as an illumination of a surprising character.

Chapter 5.

Observations on Photochemical Mechanism.

There is probably no better example of the progress of scientific thought than is reflected in the rise and fall of the various theories regarding the nature of light. As new phenomena have been discovered and our knowledge of the properties of the radiations has increased, old theories have become inadequate, and efforts have been made to provide more satisfactory explanations. The old corpuscular theory, generally accepted up to about 1800, regarded light as made up of minute particles shot off by all bodies which radiate light or heat, which produced their effects upon impact. This theory was unable to explain the facts of interference, and came to be discarded in favor of the wave theory first suggested by Huygens. Since waves must have a medium, it became necessary to postulate the existence of an "ether," possessing no mass, but pervading all matter and space. For about a century the ether theory was satisfactory in explaining all the phenomena then known, and was even able to predict a number of new effects.

The discovery that the visible portion of the solar spectrum comprised only a small fraction of the total radiant energy, led to investigations of the invisible radiations—infra-red, ultraviolet, and X-rays, particularly—which were destined to produce results of much importance from the standpoint of the theory of light. With the beginning of the twentieth century came the observation that X-rays have the power to detach and eject electrons from the molecules of gases through which they pass. In view of the fact that only a very small proportion of the molecules which the rays pass are thus affected, it is difficult to explain this phenomenon on the basis of a wave front of uniform energy. When ultraviolet rays fall on metals, electrons are likewise found to be ejected, producing what is known as the photoelectric effect. That the energy of ejection of the electron is not in any way dependent on the intensity of the incident light was first noted by Lenard,[1] and confirmed by Millikan.[1a] This again is difficult to explain in terms of the ether theory, but is understandable if a corpuscular theory is adopted.

However, the old objections to a corpuscular theory remain valid, and Thomson therefore evolved a modification of the ether hypothesis, in which the ether was supposed to have a fibrous structure. This "ether-string" theory explained the localized action of light rays in such cases as have been mentioned, and was also free from many of the objections to a corpuscular theory. The facts of interference are un-

[1] Ann. Phys. iv, 1902, *8*, 149.
[1a] Phys. Rev. 1913, *1*, 73.

explainable, as in the case of the older theory. Numerous other objections to the ether-string theory have been advanced from time to time. After a consideration of Planck's work on black body radiation, Einstein [2] assumed that a source of radiations could emit or absorb energy only in units, or quanta.[2a] The size of the quanta is proportional to the natural frequency of the emitter, and is always equal to $h\nu$ where ν is the frequency of the emitter, and h is Planck's constant. It has been demonstrated experimentally that the energy with which an electron escapes in photo-electric phenomena is always $h\nu$, and that this amount is not varied by the nature of the material or the intensity of the radiation.

Further confirmation of the quantum theory is found in the work of Compton,[3] who reasoned that light of a given frequency should be transformed to a lower one on impact with an electron. The light quantum, on striking a free (valence) electron must give up a part of its energy and recoil with a smaller amount. On account of the fact that the mass of a light quantum of even the hardest X-ray is, perhaps, of the order of one tenth of that of the electron, it is not possible for the light quantum to give up all its energy. If the light quantum collides with a "bound" electron, practically all of the energy is transferred, owing to the comparatively huge mass of the atom. This view has been experimentally proved, using X-rays from a molybdenum target, and the free electrons of graphite as the scattering substance. It was found that the α line of molybdenum shifted in approximately correct amount toward the longer wave-lengths. Compton used the ionization chamber method and Ross [4] confirmed his work, using the photographic plate; a more accurate method. Although Duane and Clark [5] were unable to agree with these results and suggest another explanation, Becker, Watson and Smythe,[6] using aluminum as a scattering medium, separated the Duane and the Compton effects and confirmed the latter.

While different investigators vary in their opinions as to the source of the energy with which electrons are emitted, Einstein's equation has been favorably considered. According to his theory, for the decomposition of a gram equivalent of a substance by a photochemical process, the amount of radiant energy needed is $Nh\nu$, where N is the number of molecules per gram molecule, h is Planck's constant, and ν is the vibration frequency of the active radiation. This is known as the photochemical equivalence law, and it merely states that one quantum of energy is absorbed for each molecule decomposed.[7, 8]

[2] Ann. Phys. (4), 1905, *17*, 132; 1906, *20*, 199.
[2a] See page 19.
[3] Phys. Rev. 1923, *21*, 483, 715; *22*, 409.
[4] Proc. Nat. Acad. 1923, *7*, 246.
[5] *Ibid.*, Feb. and Mar., 1924.
[6] Proc. Phys. Soc., Apr., 1924.
[7] Ann. Phys. (4), 1912, *37*, 832; Chem. Abs. 1913, *7*, 1654. Note comments by Mathews, Ind. Eng. Chem. 1923, *15*, 885.
[8] A short discussion of the nature of radiant energy in the light of recent advances is given by Millikan: "The Electron," Chicago, 1924.

Intimately connected with the quantum theory is Bohr's conception of the structure of the atom.[9] According to this hypothesis, the electrons revolve about a positive nucleus in orbits of different radii. While a detailed discussion cannot be entered into here it may be stated that the emission and absorption of energy quanta are supposed to take place when the electrons jump from one orbit to another.

Many views have been presented in the attempt to explain the mechanism by means of which light facilitates reaction. Baly and Rice [10] propose a theory which considers ordinary molecules as condensed systems which are non-reactive until opened up, and discuss the relation of absorption bands and fluorescence phenomena to this process.

The positive temperature coefficients of most chemical reactions are too great to be explained by the mere increase of kinetic energy of the reacting molecules. It has often been assumed that molecules must be activated before they can react, and that this process is the one influenced by temperature increases. These considerations have led to the formulation of a general radiation theory of chemical reaction, according to which radiation, either invisible or visible, accomplishes the activation of the molecules. Trautz,[11] W. C. M. Lewis,[12] Perrin,[13] and others uphold this theory, holding that in thermal reactions the necessary energy is supplied by the black body radiation (principally infra-red) of the walls of the containing vessels. From the temperature coefficient of the reaction velocity the wave-length which should activate a given molecule may be calculated.

The radiation theory has been opposed by Langmuir,[14] Lindemann,[15] and Tolman,[16] who maintain that the amount of radiant energy available is insufficient to produce the results ascribed to it, and further point out that many substances fail to show absorption bands in the regions necessary for the absorption of radiant energy of the wave-length calculated from the theory. The last mentioned advocates a modification of the theory which overcomes some of the objections. Lewis and McKeown [17] defend the theory, claiming that it is necessary to emphasize the distinction rather than the resemblance between thermal and photochemical reactions. They define a reaction as *photochemical* when the temperature of the radiation is greater than that of the material on which it acts. It is *thermal* when the temperatures of the radiation and matter are identical.

It is not pertinent to a work of this scope to discuss at length the experimental and mathematical evidence upon which the general radiation theory of reaction is founded, but since in the special case of

[9] Phil. Mag. 1913, *26*, 1, 476, 857; 1915, *29*, 332; 1915, *30*, 394.
[10] J. Chem. Soc. 1912, *101*, 1475.
[11] Z. wiss. Phot. 1906, *4*, 160.
[12] J. Chem. Soc. 1918, *113*, 471.
[13] Trans. Far. Soc. 1922, *17*, 546.
[14] J. Am. Chem. Soc. 1920, *42*, 2190.
[15] Phil. Mag. vi. 1920, *40*, 671.
[16] J. Am. Chem. Soc. 1921, *43*, 269.
[17] *Ibid.*, 1288.

photochemical reactions there can be little doubt of the importance of the absorption of radiant energy, mention of the broader aspects of the general theory has been included. Particular aspects of some reactions in which radiations other than ultraviolet play a part, will be presented, when these offer analogy to, or confirmation of, the theories of ultraviolet action.[17a]

The interaction of ions, formed by the loss of electrons through the action of light, was at one time believed by Bodenstein to account for photochemical reactions. Later he adopted the view of Stark,[18] who held that the primary effect of light is the loosening of valence electrons, rendering the molecule chemically active. Bodenstein [19] classifies photochemical reactions as primary and secondary. Primary reactions are characterized by proportionality between the quantity of reaction and the quantity of absorbed energy, absence of influence of foreign substances, absence of influence of temperature, and by the fact that one molecule reacts for each quantum, or small number of quanta, of energy absorbed. Secondary reactions may show an excess over or deficiency from the requirements of Einstein's equation. Bodenstein also assumes that activated molecules do not lose their energy increment upon combining, but produce an activated compound which is capable of imparting its energy to other molecules.

A substance which is acted upon by the primary product of a photochemical reaction is known as an *acceptor*. To measure a reaction accurately the acceptor must be such that it reacts at a rate equivalent to that of the primary reaction. The photochemical reactions between bromine and cyclohexane, and between chlorine and

[17a] Concerning trends in photochemical research, Mathews, loc. cit., very pointedly remarks that the radiation hypothesis furnishes the present battle ground of most interest, and rightly so, because once we learn the ultimate relation between chemical activity and frequency, many of our other problems will at once be solved. He charges that the original form of the photochemical equivalence law of Einstein, based upon the quantum theory, is so rarely in accord with observed facts as to render it of little value in itself. Any law which has its sole foundation in the quantum theory of Planck is bound to be a subject for considerable dispute, inasmuch as this theory itself is by no means fully accepted by many physicists. To those who do not accept the quantum theory, the failure of the Einstein law and the radiation hypothesis of Lewis-Perrin is naturally the fulfilment of the expected. Assuming the validity of the quantum theory, we soon find ourselves in other difficulties. The Einstein law is supposed to apply only to the *primary* light reaction, and the difficulty is that the total amount of reaction as measured may be not just the amount of primary reaction which takes place, but may be either greater or less than that amount, due to secondary reaction or reactions. It therefore becomes necessary to find a secondary reaction which is exactly equivalent to the primary one, since the latter can itself rarely be measured quantitatively. A substance which will react with the product of the primary reaction quantitatively so as to give a true measure of the primary reaction, is called an "acceptor," and the problem resolves itself into finding suitable acceptors for the reactions to be studied. The Lewis-Perrin radiation hypothesis, while appearing to be somewhat more hopeful than the original formulation of Einstein, has been shown to have many weaknesses and certain apparently insuperable difficulties, according to some critics.

[18] Atomdynamik 1911, II., 207.

[19] Z. Phys. Chem. 1913, *85*, 333.

trichlorobromomethane have been investigated by Noddack.[20] In the former case a slow reaction takes place in the absence of light. Trichlorobromomethane is found to be a good acceptor for activated chlorine molecules, no recognizable change taking place in the dark after forty days at 37° C., but some reaction occurs at 100° C. in several hours.[21] Both reactions follow the Einstein photochemical equivalence law. In the case of the reaction between chlorine and trichlorobromomethane it is found that admixture with carbon tetrachloride lowers the photochemical effect with increasing dilution. This phenomenon is ascribed to the energy loss of the activated molecules owing to collisions with indifferent carbon tetrachloride molecules. The explanation according to Bohr's theory is as follows: a quantum $h\nu$ is absorbed by the chlorine molecule, the valence electron springs to a larger ring, and the molecule is activated. This active state has a given "life" (calculated as 10^{-10} seconds), during which it may react with an acceptor. If no acceptor is present, the activated molecule gives up energy in the form of other quanta (luminescence or heat), or transfers it to indifferent molecules, causing a general rise in temperature. Illumination of the mixture: chlorine, trichlorobromomethane, carbon tetrachloride, represents a limiting case of pure photochemistry, and in it the light energy is converted partly into chemical energy and partly into heat.

Pusch [22] finds hydrogen to be an unsuitable acceptor in its reaction with bromine, the amount of reaction found being much less than that expected from theory. Using solar radiation, in one experiment only .02 g. of bromine combined instead of 2.3 grams. It will be shown later that Nernst accounts for this behavior thermodynamically. Using a "Nitra" lamp (nitrogen-filled), heptane, hexane, and toluene all combine with bromine at a rate greater than that required by the theory, but hexahydrobenzene is a suitable acceptor.

Several investigators have noticed that in the photochemical reaction between hydrogen and chlorine, the extent of reaction far exceeds that expected from the quantity of energy absorbed. Nernst,[23] using a thermodynamical treatment, explains the multiplied secondary reaction by the following cycle:

$$\mathrm{Cl} + \mathrm{Cl} = \mathrm{Cl_2} + 106{,}000 \text{ cal.}$$
$$\mathrm{H} + \mathrm{H} = \mathrm{H_2} + 100{,}000 \text{ cal.}$$
$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H} + 25{,}000 \text{ cal.}$$
$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl} + 19{,}000 \text{ cal.}$$
$$\text{and} \quad \mathrm{H} + \mathrm{Cl} = \mathrm{HCl} + 125{,}000 \text{ cal.}$$

The spectral region of the light which can dissociate chlorine molecules into atoms as calculated from the quantum theory agrees with that known to cause combination of hydrogen and chlorine. Nernst considers that this justifies the assumption of free chlorine atoms for the

[20] Zeitsch. Elektrochem. 1921, *27*, 359; J. Chem. Soc. 1921, *120*, ii, 568.
[21] See Von Rancke, J. Chem. Soc. 1921, *120*, ii, 580.
[22] Z. Elektrochem. 1918, *24*, 336.
[23] Sitzb. Berlin. Akad. Wiss. 1911, 65

propagation of the photochemical reaction. The combination of the chlorine atom with the hydrogen molecule, and the splitting of the unstable product into hydrogen chloride and a free hydrogen atom, gives a large heat evolution, and is therefore in the direction of spontaneous reaction. When the free hydrogen atom just produced reacts with a chlorine molecule, the reaction is again of the same nature. The chlorine atom liberated brings back the original system, which can repeat indefinitely except for the cross reaction of the hydrogen and chlorine atoms. Nernst calculates that a similar cycle of hydrogen and bromine is impossible on account of the negative heat of reaction (— 15,000 cal.). A mixture of hydrogen and bromine vapor is not light sensitive at ordinary temperatures.

In studying the photochemical reaction of iodine with potassium oxalate, Berthoud and Bellenot [24] noted that 25 molecules of iodine react per quantum of blue light absorbed. They explain this by means of a chain of reactions similar to that described above for hydrogen and chlorine.

Weigert [25] observes that when gaseous systems containing chlorine are exposed to light, molecular complexes are probably produced, which act catalytically as reaction nuclei. At these nuclei, it may be supposed, equilibrium between the reacting gases is established with such rapidity that the further progress of the reaction is conditioned by the rate of diffusion to these nuclei of the remaining portions of the gases. According to this theory, therefore, photochemical reactions may be brought under the category of heterogeneous reactions. Experimental evidence is brought forward showing that when chlorine is exposed to ultraviolet rays, violet or blue light, the production of fog may be actually observed. If Weigert's view is correct, then reactions which are not themselves affected by light should be catalytically affected by the presence of the reaction nuclei already mentioned. In this connection, it is shown that the formation of water, the formation of sulfur trioxide, the dissociation of carbonyl chloride, the decomposition of ozone, the Deacon chlorine process, and the formation of ammonia from its elements are reactions which, although not themselves sensitive to light, may be sensitized by adding chlorine and exposing to light. The fact that all photochemical reactions known to Weigert were unimolecular, and that the temperature-coefficient of these reactions was of the same order as the temperature-coefficient of a diffusion process is regarded as lending support to the conception of photochemical reactions as heterogeneous catalytic reactions. That the activity of chlorine and other substances sensitive to light does not cease immediately when exposure is stopped is also in favor of the foregoing view that definite nuclei are produced.

Baly and Barker [26] also studied the photochemical reaction between hydrogen and chlorine, at constant concentration and with varying light intensity. With a given intensity the amount of hydrogen chloride

[24] Helvetica Chim. Acta. 1923, *7*, 307.
[25] Ann. Physik. 1907, iv, *24*, 243.
[26] J. Chem. Soc. 1921, *119*, 653.

formed in unit time is at first small, and then rapidly increases up to a constant maximum; this constant maximum rate is not proportional to the intensity of the light, but the divergence from Einstein's law of photochemical equivalence depends on the intensity of the light, and rapidly increases therewith. The expansion of chlorine observed when it is illuminated is proportional, not to the intensity of the light but to the rate of the reaction. This expansion is not noticed during the induction period which is always observed when volatile nitrogen compounds are present. In the absence of these compounds, the expansion is always observed as soon as the activating light falls on the mixture of hydrogen and chlorine. As has already been explained the velocity of reaction steadily increases with constant light intensity up to a constant maximum. If the light rays be cut off at any moment, the contraction in volume may be measured and it is found that the expansion first observed and the contraction noted afterward are proportional to the rate of combination. Whatever may be the explanation of this expansion, whether it be due to a dissociation of some of the molecules of chlorine into atoms, or whether it be a purely thermal effect due to degradation to heat of light absorbed, it is obvious that it is increased by the absorption by the chlorine of the energy radiated by the hydrogen chloride. The expansion is observed when the light is deprived of infra-red rays by passage through a layer of water two inches thick, and it is not observed when the ultraviolet rays are removed by interposing a solution of iodine in carbon disulfide. There is no doubt, according to Baly and Barker, that the expansion of the chlorine, and its activation are due to the absorption of light of frequencies lying within its ultraviolet absorption band. This band has its center at 333 μμ (3330 Å), and when the chlorine is at atmospheric pressure it extends from about 400 μμ to 270 μμ (4000 to 2700 Å).

The divergence from Einstein's law has previously been suggested as being due to the reabsorption by the reactant molecules of the energy radiated by the resultant molecules. This reabsorption depends on the concentration of the reactants with constant illumination, and on the intensity of the light with constant concentration.[27]

As noted above, in the photochemical combination of hydrogen and chlorine, the first change is a volume change which reverses as soon as the illumination is removed. This change, the so-called Draper effect, has been examined by Weigert and Kellermann,[28] who show that it is due to a warming of the gas, and not as has been often suggested, to a primary splitting of the chlorine molecule into atoms. The amount of the thermal expansion of chlorine electrolytic gas corresponds with the amount calculated from the amount of hydrogen chloride produced by the photochemical reaction and the heat liberated thereby. Electrolytic gas which has been dried with sulfuric acid

[27] It may be noted that Slade and Higson (Proc. Roy. Soc. A. 1920, *98*, 154) have obtained similar results in experiments using photographic plates, finding that the amount of silver is not proportional to the intensity of the light.

[28] Z. Physikal. Chem. 1923, *107*, 1; see also Weigert, Z. Elektrochem. 1922, *28*, 456.

shows the Draper effect immediately on entry into the irradiation vessel. After the addition of liquid water, the effect is not shown so strongly as with the dry gas until it has been shaken with the water for a long time. In the case of spark illumination in the presence of liquid water, the Draper effect produced by the first spark has quite a different form from that produced by the subsequent sparks. After the first momentary expansion of the gas, a second much slower dilation commences, and then only the liquid thread of the manometer takes up a position beyond its original position. This final contraction corresponds with the absorption of the hydrogen by the confining water. After all the succeeding sparks, the gas contracts after the first expansion impulse in the normal way. The meaning of the second, slower, expansion with the first spark is probably to be found in the heat of condensation of liquid drops of hydrochloric acid from the water vapor contained in the gas. The hydrogen chloride produced by the subsequent sparks comes, therefore, only into contact with water vapor at a much lower tension, and is condensed in the confining water which absorbs the heat of condensation.

Using the Töpler cloud method these investigators find that with continuous irradiation a cloud is produced in sensitive chlorine electrolytic gas immediately. The cloud is developed only when the gas—chlorine, chlorine electrolytic gas, or bromine vapor—is irradiated with light of short wave-length, and the strength is parallel with that of the simultaneously observed Draper effect. From further experiments along this line it is concluded that the observed combination of chlorine and hydrogen in light is for the most part a purely chemical process, although the first impulse is furnished by light. After this first impulse, in the space of about .01 second, the reaction develops into a purely chemical process in the dark. The dark reaction, however, is made up of a series of successive processes, and the time elapsing before the maximum is reached with the more sensitive gas mixtures shows that in these cases the passage through the series of reactions takes longer than with the less sensitive gas mixtures.

Hydrogen and chlorine, in admixture, do not react when screened from light but when exposed to rays of frequencies within the ultraviolet absorption band of chlorine the two gases at once begin to unite.[29] The chlorine molecules, inactive in the dark, are activated by the absorption of energy, the minimum amount per molecule being $9 \times 10^{14} \times 6.56 \times 10^{-27} = 5.91 \times 10^{-12}$ ergs, where 9×10^{14} is the central frequency of the absorption band, v, and 6.56×10^{-27} is Planck's constant h. These activated molecules then react with the inactive hydrogen molecules, and it would seem that this process must be accompanied by a transfer of energy from the former to the latter. Whatever may be the actual mechanism of the process, the net result is the dissociation of the hydrogen molecule to form molecules of hydrogen chloride, and the energy necessary for this dissociation must have been derived from the activated chlorine molecules. These investigators consider that this transference of energy can only be

[29] Baly and Barker, loc. cit.

possible if the hydrogen and chlorine have frequencies in common; that is either the frequencies of the chlorine must be exact integral multiples of the fundamental atomic frequency of hydrogen, or the frequencies of both must be exact integral multiples of some universal fundamental unit.

It appears that the frequencies characteristic of the hydrogen chloride molecule are exact integral multiples of both the fundamental atomic frequency of hydrogen, and the fundamental atomic frequency of chlorine. Considerable support is thereby gained for the conclusions drawn from spectroscopic observations, that the true molecular frequency of a compound molecule is the least common multiple of the atomic frequencies of its component atoms.

A new type of photocatalysis is indicated, whereby a reaction can be photochemically induced by light which is not absorbed by the reactants, but is absorbed by the photocatalyst.

To cause a molecule to undergo a specific reaction, as pointed out by Baly and his co-workers,[30] requires a definite amount of energy. This may be supplied either as one quantum at the ultraviolet frequency, or as several quanta at the infra-red frequency characteristic of the molecules or atoms involved. A reaction is defined as *photochemical* when the energy is absorbed at ultraviolet frequencies. It is possible to cause a substance A to undergo a photochemical reaction in light of a frequency not absorbed by that substance, if a substance B, having the same infra-red frequencies as A, be mixed with it. When the two are exposed to light absorbed by B and not by A, then the energy radiated by B in the infra-red will be absorbed by A, resulting in the latter undergoing a reaction of a type similar to that above defined as photochemical. B then acts as a photocatalyst and the reaction is *photocatalytic*.[31] The defining criteria for a photocatalyst are that it must have exactly the same infra-red frequencies as the catalyte, and a frequency different from that of the catalyte in the visible and ultraviolet regions. According to Baly,[32] the fundamental molecular frequency is usually in the short infra-red of wave-length between 10 μ and 3 μ (100,000 and 30,000 Å), while the atomic frequency is in the extreme infra-red of the order of 1.5×10^{11} or wave-length 2000 μ (20,000,000 Å).

An instance of photocatalysis is reported by Daniels and Johnson.[33] The decomposition of nitrogen pentoxide at 0 deg. C. is a monomolecular gas-phase reaction, in which the black body radiation of the walls of the vessel causes a rate of reaction which is negligible in comparison with that produced by radiation received from a body emitting white light, and not in equilibrium with the system.

[30] Baly, Phil. Mag. 1920, *40*, 1, 15; Baly, Heilbron and Barker, J. Chem. Soc. 1921, *119*, 1031.

[31] It must be remembered that the term "photochemical reaction" is very often used in a sense much broader than the above definition would imply, being frequently applied to any reaction facilitated by visible or invisible radiation, regardless of the presence or absence of photocatalytic substances.

[32] Tr. Far. Soc. 1922, *17*, 588.

[33] J. Amer. Chem. Soc. 1921, *43*, 72.

Calculations from the reaction velocities at different temperatures, according to the Lewis and Perrin theories,[34] indicate that a wave-length of 1.16 μ (11,600 Å) should cause the reaction to proceed. Rays of this wave-length, however, do not decompose nitrogen pentoxide within the limits of experimental observation. Light in the region 400-600 μμ (4000 to 6000 Å) accelerates the decomposition, but only in the presence of nitrogen dioxide. The autocatalytic effect of the dioxide in the dark is negligible.

These investigators propose a mechanism for the catalytic effect of the nitrogen dioxide which is very similar to the one outlined more elaborately by Baly and his co-workers.[35] They conceive that the dioxide absorbs blue light over a wide range, and through fluorescence passes it out in the infra-red region, where its lines overlap those of the pentoxide, thus causing the decomposition of the latter. It is suggested that other chemical reactions may be brought about by catalysts which absorb radiant energy over a wide range, and emit it in a narrow region where it is effective.

The facts of this reaction also give a concrete picture of at least one kind of an induction period. The decomposition of pure nitrogen pentoxide at 0 deg. C. is so slow as to be barely detectable, but eventually sufficient dioxide forms to give, when illuminated, a fairly rapid reaction.

The photochemical decomposition of chlorine monoxide has been investigated by Bowen [36] whose results indicate that two molecules are decomposed for each quantum absorbed. Two alternative and indistinguishable mechanisms explain this phenomenon.

Either the decomposition is unimolecular,

$$Cl_2O + h\nu \rightarrow \text{"active" } Cl_2O \rightarrow Cl_2 + O,$$

this being the only possible unimolecular decomposition in violet light and is followed by a spontaneous reaction,

$$Cl_2O + O \rightarrow Cl_2 + O_2 + 91{,}000 \text{ cal.},$$

or the change is

$$Cl_2O + h\nu \rightarrow \text{"active" } Cl_2O,$$

followed by

$$\text{"active" } Cl_2O + Cl_2O \rightarrow 2Cl_2 + O_2 + 95{,}000 \text{ cal.}$$

Both possibilities satisfy the condition that the spontaneous reactions shall be exothermic. Bowen notes that the very large heat evolutions in either case do not lead to further decomposition, as would be expected if the views of Baly [37] that this energy would be liberated at infra-red frequencies capable of re-absorption, are correct.

When chlorine peroxide is exposed to light a more complex decomposition takes place, with formation of large quantities of an unstable brown liquid. This disappears with formation of white fumes

[34] J. Amer. Chem. Soc., 1921, *43*, 72.
[35] Loc. cit.
[36] J. Chem. Soc. 1923, *123*, 2328.
[37] Loc. cit.

when a trace of water vapor is admitted. Traces of white fumes are also observed when chlorine monoxide which has been exposed to light is allowed to come into contact with moist air. It seems that in both cases some formation of other oxides of chlorine occurs besides the simple decomposition.

The complex photochemical relationships of the hydrogen halides are discussed by Bowen [38] with reference to the theory that dissociation into atoms occurs, e.g., $Cl_2 + h\nu = Cl + Cl$, or $HI + h\nu = H + I$; and also the theory that active molecules are produced. He shows that the dissociation theory affords a quantitative explanation of all the experimental observations, if due consideration is given to the heats of reaction, and if it is assumed that a large heat evolution favors spontaneous reaction, while heat absorption has the opposite tendency. This explanation is not possible on the basis of the activation theory.

Rideal and Hawkins [39] state that the hydrolysis of methyl acetate in aqueous solution is accelerated by infra-red radiation, and that the spectral region of photoactivity is in agreement with that calculated on the activation and quantum theories of chemical action. Taylor [40] comments on the opacity of water to the infra-red, and points out that, under the conditions of Rideal and Hawkins' experiments, only the surface layers could have been irradiated. If the effects are actually as indicated, the influence of infra-red radiation is enormous.

In the application of the Einstein law of photochemical equivalence it has been assumed that the absorption of energy takes place by quanta in single molecules, as in the Bohr atom, the energy of the molecules being increased thereby. The passage of a single electron to an orbit of higher quanta has been assumed to be the first step in a true photochemical process. In order to remove some of the difficulties which result from this conception of photochemical transformations, Weigert [41] assumes that not a single molecule, but a system of two molecules or molecular parts participates in the process of absorption. The distance between these two molecules can be bridged over by an electron in a photoelectric effect. In order that an absorbing system consisting of separated "electron-givers" and "electron-receivers" may be photochemically sensitive, the positive or negative molecular ions formed in the inner photoelectric effect need not be wholly stable, but there must be the possibility of a supplementary decomposition or another reaction. Since both an "electron-giver" and an "electron-receiver" are necessary for the formation of molecular ions, it is not correct, strictly, to speak of a photosensitive substance, but only of a photosensitive system. The fact that the separation of electrons is a primary process justifies the importance of the "electron-giver" in photochemical reactions.

The spacial distribution of the "electron-givers" is concerned with

[38] J. Chem. Soc. 1924, *125*, 1233.
[39] J. Chem. Soc. 1920, *117*, 1288.
[40] J. Ind. Eng. Chem. 1921, *13*, 77.
[41] Z. Physik. Chem. 1922, *102*, 416.

the absorption spectrum and therefore also with the sensitiveness spectrum of the photochemical reaction. The primary change of a photosensitive system, that is, the origin of positive and negative molecular ions, or the rearrangement of electrons in a single molecule, is the same qualitatively for all spectral regions in which the process occurs. This is effected according to the spacial separation of the "giver" and the "receiver" through different energy quanta *hv*. The closer the "giver" and the "receiver" stand to one another, the smaller is the number of quanta necessary. These quanta may be less than the energy calculated from the heat of reaction of the primary process of the elementary change. This representation has certain advantages over that hitherto employed, which requires that a single molecule in different regions of a wide absorption band take up different amounts of energy, while the actual resultant chemical process is always the same. The hypothesis has led to the assumption of a division of the absorbed energy into chemical and thermal.

According to the new "dualistic" hypothesis, each constellation of "electron-givers" and "electron-receivers" absorbs during the process of absorption only the quantum with which it is in tune, so that a partition of the energy quanta, which is in contradiction to the fundamental conception of the quantum theory, is not necessary. Whether the quantum of energy received from the "electron-giver" is employed chemically or thermally depends on whether the "electron-receiver," after its transition to a negative molecular ion, is capable of further change or is stable. Since in all cases both kinds of "receivers" are present at the outset, and since those capable of change rapidly diminish, the yield of a photochemical reaction decreases with the duration of the radiation.

Bodenstein and Bonhoefer [42] have noted that the decomposition of ozone by ultraviolet rays in the presence of chlorine as a photocatalyst is not disturbed by the products formed, and follows Einstein's photochemical equivalence law. This, together with the fact that the velocity of the reaction is independent of the concentration of the ozone, shows, according to Weigert,[43] that an upper limit of the ozone concentration exists, at which the whole of the light energy absorbed by the chlorine is converted into chemical energy. The same is found to be the case for the activation of hydrogen sensitized by mercury vapor. Because, however, of the low absorption and low extinction values for chlorine, the ozone reaction occupies the entire vessel and reaches at a low pressure of ozone the limiting value above which all the energy absorbed by the chlorine is transformed into chemical energy. For the activation of hydrogen, the absorption and extinction by mercury are high and the reaction is close to the walls, so that fifty times greater pressure of hydrogen must be reached before the limiting saturation value is obtained. For ozone this pressure is 0.5 mm. and for hydrogen, 10 mm. of mercury, and their relation to the pressure of the sensitizing molecules (chlorine, ½ atmosphere; mercury, 0.009 mm.)

[42] Z. Physik. 1923, *13*, 94.
[43] Z. Physik. Chem. 1923, *106*, 407.

are widely different. The ratio of the number of reacting molecules to the number of molecules of the sensitizing agent for the chlorine—ozone reaction is 1.3×10^{-3}, and for the hydrogen-mercury reaction it is 1.1×10^{3}. If, on the other hand, the number of molecules in calculated in layers which produce the same amount of weakening of the radiation, they will be found to be the same in the two reactions. It is therefore likely that in both processes the initial stage is the same.

The hypothesis is advanced that the radiation absorbed by the excited molecules is at first re-emitted as resonance radiation in the normal manner, and that this absorption and emission process is repeated so often that at last the absorption leads, in a binary absorption system, to an internal photoelectric effect, whereupon a chemical process or a translatory displacement of the particles follows. Whereas the resonance radiation with mercury, on account of the extremely strong absorption of the mercury vapor for the exciting resonance line, is easily observed, this can hardly be expected in the case of chlorine with its hundred million times smaller absorption constant. But there are indirect reasons for the non-thermal absorption of pure chlorine. The thermal increase in volume during the radiation is only to be observed in the presence of moisture or other impurities. According to this view the transformation of the absorbed energy to the chemically reacting system does not occur simultaneously with the absorption of the radiation; the process requires, on account of the repeated absorption and emission of a once-absorbed energy quantum, a definite time before it is completed. The energy quantum remains, in a sense, in the reacting system until entirely used up.

The photochemical chlorine-hydrogen reaction shows a retardation of about .01 second. It is not, however, certain that this measured delay is due to the above effect, since the yield in this reaction is much greater than Einstein's law demands. The delay can also be explained by assuming a long chain of reactions. (See Bodenstein, *loc. cit.*) A special photoelectric effect is assumed, which may represent the primary process by which the chlorine-hydrogen reaction is started. This assumption does away with the necessity of assuming excited chlorine molecules, and a splitting of the molecules into atoms. Weigert points out that it may be concluded that ozone will be decomposed by ultraviolet rays of long wave-length, in the absence of any other substance, and that perhaps the radiation absorbed by the chlorine falls in the ozone absorption band, and that during the repeated absorption and re-emission it is used up in this weak absorption region.

Kornfeld[44] designed an experiment to test Weigert's theory of the transformation of radiation in chemical reactions. In order to determine whether reaction is effected by re-emitted radiation, such as is said to be re-emitted by chlorine in the ozone reaction described above, the formation of carbon dioxide from carbon monoxide and oxygen in the presence of carbonyl chloride and light, was investi-

[44] Z. Physik. Chem. 1924, *108*, 118.

gated. A quartz tube, containing carbonyl chloride, carbon monoxide, and oxygen, was surrounded by a second tube with quartz ends, containing carbonyl chloride. When the apparatus was submitted to the action of light, it was found that no combination of the oxygen and carbon monoxide occurred in the inner tube. This, according to Kornfeld, demonstrates an error in the assumptions made in Weigert's hypothesis, and furnishes further proof of the sensitization of the reaction between oxygen and carbon monoxide by kinetic means.

Luther and Goldberg [45] have shown that oxygen acts as an inhibitor in all photochlorinations, and they consider that the effect is due to absorption by oxygen of radiation re-emitted by the chlorine, which would promote the reaction if not thus absorbed. Bodenstein extends the inhibiting effect of oxygen to all secondary photochemical reactions, except those in which oxygen itself takes part.[46]

The influence of moisture in modifying the rate of thermal and photochemical reactions has been the subject of many researches, and led to the publication of conflicting results. Coehn and Tramm [47] investigated the action of ultraviolet rays on dry and moist mixtures of carbon monoxide and oxygen. Moist mixtures exploded; moderately dry mixtures were not explosive but inflammable; strongly dried mixtures were neither explosive nor inflammable, when heated. All three mixtures combined in about equal amounts when irradiated with ultraviolet rays, forming carbon dioxide, and not formic acid, as is the case in the thermal reaction at high temperatures in the presence of moisture.

Baker [48] observed that mixtures of hydrogen and oxygen which have been desiccated by prolonged contact with phosphoric oxide can be heated to redness in Jena glass tubes without the occurrence of an explosion. On the other hand, according to Coehn and Tramm,[49] the presence of moisture does not appear to exert an appreciable influence on the rate of combination of hydrogen and oxygen when exposed to the ultraviolet rays of the Heræus lamp.

The same workers [50] exposed moist and dry mixtures of chlorine and hydrogen in quartz tubes to the light of a 100-candle-power Osram lamp. Under identical conditions the union of the gases in the presence of moisture occurred quantitatively within 12 minutes, whereas in the dry mixture there was no sign of combination after 2 hours.

Coehn and Jung [51] show that under similar conditions, union is quantitative within twelve minutes under the influence of ultraviolet rays. The wave-length of the active rays is less than 254 μμ (2540 Å).

The rate of decomposition of hydrogen bromide or hydrogen iodide under the influence of ultraviolet radiation appeared not to be affected

[45] Z. Physik. Chem. 1906, *56*, 43.
[46] See also Bodenstein and Dux, Z. Physik. Chem. 1913, *85*, 297.
[47] Ber. 1921, *54 B*, 1148.
[48] J. Chem. Soc. 1902, *81*, 4000.
[49] Ber. 1923, *56 B*, 455.
[50] Ber. 1923, *56 B*, 458.
[51] Ber. 1923, *56 B*, 696.

by the presence of moisture,[52] whereas hydrogen chloride did not suffer decomposition if thoroughly dried. The velocity of combination of carbon monoxide and chlorine was greatly reduced by thorough desiccation, but the process invariably took place at an appreciable rate. Reaction in the case of sulfur dioxide and chlorine was completely inhibited by protracted drying of the gases.

[52] Coehn and Tramm, loc. cit.

Chapter 6.

Reactions of Gases in Ultraviolet Rays.

That many gases, as well as solid substances and liquids, are affected by light and particularly by ultraviolet radiations was noted early in the course of photochemical experiments. Changes both in electrical properties and in chemical reactivity were found to take place under the influence of light, and some attempts to correlate the two are described in the present chapter.[1]

The theoretical importance of refraction and dispersion of gases has been increased by work on molecular structure. Data for air have great practical value and Traub [2] shows that previous observers are in rather wide disagreement in their results on air, especially for ultraviolet. Warburg,[3] working at pressures of 30 to 400 atmospheres, found large deviations from Beer's law. The molecular absorption of oxygen increases appreciably with the pressure. The increase is greater for the short than for the long waves, and is greater in pure oxygen than in mixtures of oxygen and nitrogen. The deviations are ascribed to molecular collisions. Thompson [4] exposed various gases to the action of ultraviolet rays and observed the effect of this exposed gas on an electroscope. When exposed to ultraviolet rays, air increased the natural leak eight times, carbon dioxide sixteen times and ammonia over one hundred and fifty times. The rays which produce this ionization are absorbed by a few millimeters of air.

Measurements of the atmospheric ionization and the mobility of the atmospheric ions at different altitudes were taken by Wigand [5] during balloon ascensions and aëroplane trips, altitudes of four and five kilometers being attained. In the lower regions where clouds, dust, and haze exist, no increase in the ions was noted, but above three kilometers the number of ions increased to several times the number noted at the surface. The results are accounted for by the fact that as the surface of the earth is left, the effect of the radioactive elements becomes lessened and also that the moisture and dust serve to recombine the ions, but at the higher altitudes the ultraviolet rays from the sun have no effect in causing them to combine.

[1] Some gaseous reactions are also discussed in Chapter 5.
[2] Ann. Physik. 1920, *61*, 533; Chem. Abs. 1920, *14*, 2297.
[3] Sitzungsber. Preuss. Akad. Wiss. Berlin, 1915, 230; J. Chem. Soc. 1920, *118*, *ii*. 404.
[4] Proc. Camb. Phil. Soc. 1907, *14*, 417.
[5] Physik. Z. 1921, *22*, 36; Chem. Abs. 1921, *15*, 1249.

It has been observed by Slatineanu [6] that the reaction between a gas and another substance is facilitated by subjecting the gas to the action of ultraviolet radiation, Lenard, Becquerel or Röntgen rays and then bringing it into contact with a metallic surface, or by directing the gas on to a metallic surface which is itself subjected to the action of ultraviolet or other rays. By subjection to the action of these rays, the gas is stated to emit cathode rays whose vibrations are amplified by contact with a metallic surface.

The dissociation of hydrogen in low-voltage arcs was observed by Duffendack and Compton [7] not to take place below a minimum voltage of 13 but above 16 volts the rate was rapid, decreasing to 65 volts. Dissociation from contact with the hot filament was always superimposed on the electrical dissociation. With mercury arcs, the dissociation was several times more rapid, the hydrogen molecules presumably being activated by excited mercury atoms.

Dickinson [8] notes that hydrogen and oxygen in contact with mercury combine to form water at 45° C. or even at room temperature, when illuminated by rays from a quartz mercury arc lamp cooled by a blast of air. This is said to be due to dissociation of the hydrogen by collisions with mercury atoms excited by absorption of the mercury line 253.7 μμ (2537 Å).[9] In the absence of any one of the three substances or of the exciting radiation, no reaction takes place.

Experiments with mixtures of hydrogen and oxygen have been conducted by Thiele [10] with moist gases, with gases dried by means of sulfuric acid, and with gases dried by contact for eighteen days with phosphorus pentoxide. Combination between the two gases is accelerated by ultraviolet radiation from a high tension Heræus mercury lamp (E.M.F. 120 volts). The presence of moisture was not essential, the reaction velocity being indeed somewhat greater with dry than with moist gases.

Owing to modifications produced in the molecules the refractivities of certain gases should be different under the influence of ultraviolet from what they are in the normal case. To test this Smith [11] placed a tube containing hydrogen, nitrogen and mercury vapor successively in one path of a Jamin interferometer and the fringe movement consequent on shutting off ultraviolet rays which had been exciting the gas for a given time was noted. Results show increases in refractivity of hydrogen and nitrogen on shutting off the rays, indicating dissociation into atoms. Mercury most often showed a decrease, possibly owing to the formation of a diatomic molecule.

The formation of hydrogen peroxide from water and oxygen in ultraviolet rays could be observed only occasionally and appeared to depend largely upon experimental conditions, possibly upon the presence of impurities.

[6] Chem. Abs. 1921, *15*, 988; British Patent 154,213, 1920.
[7] Phys. Rev. 1924, *23*, 583.
[8] Proc. Nat. Acad. Sci. 1924, *10*, 409; J. Chem. Soc. 1924, *126, ii*, 841.
[9] See Cario and Franck, J. Chem. Soc. 1922, *122, ii*, 809.
[10] Z. angew. Chem. 1909, *22*, 2472.
[11] Trans. Roy. Soc. Canada 1923, *17*, 63; Science Abstracts *27 A*, 613.

Baskerville,[12] discussing the use of ultraviolet light in the laboratory and in practice, observes that one very marked property of ultraviolet radiation is its power to transform *oxygen* into *ozone*. This takes place best at low temperatures. It has been thought that the ultraviolet from the sun forms ozone in the upper atmosphere which then settles down and oxidizes the impurities nearer the earth. From a series of experiments on the origin of atmospheric ozone Henriet and Bonyssy [13] also conclude that ozone is formed at the expense of the oxygen of the high regions of the atmosphere under the influence of the ultraviolet rays of the sun and is carried to the lower layers of the air by winds and rain. They found the proportion of ozone in the air is at a maximum during a West or Southwest wind and at a minimum during an East wind, and it is also increased during clear, calm weather by the direct action of the solar radiations on the lower layers of air.

Fabry and Buisson [14] have made determinations of the variations of the constant of absorption for ozone. From these results, combined with measurements made on the amount of light from the sun transmitted by the atmosphere, Fabry and Buisson draw the conclusion that the ozone content of the atmosphere, if evenly distributed would be equal to 0.6 cubic centimeters per cubic meter of air. Hallwachs [15] has shown that small quantities of ozone can be estimated photoelectrically by reason of the large specific absorptive power of the gas for ultraviolet radiation of wave-length in the neighborhood of 285 μμ (2580 Å). For such measurements the pressure of the gas in the absorption tube should be of the order of 0.01 mm. of mercury. On the assumption that the photoelectric effect is proportional to the intensity of the incident light, Krüger and Mueller [16] have measured the absorption of ultraviolet of wave-length 254 μμ (2540 Å) in ozonized oxygen with the aid of a photoelectric cell containing a potassium electrode in contact with hydrogen at a pressure of 0.3 mm.

When a tube of fused quartz was exhausted until the pressure registered only a few millimeters and the discharge from an induction coil passed through it, Goldstein [17] observed an intense odor of ozone in the surrounding atmosphere, and iodized starch paper was turned blue quickly. The odor of ozone was not perceptible when the pressure inside the tube exceeded a certain value. The phenomenon is ascribed to the ultraviolet rays of short wave-length penetrating the quartz and then converting the atmospheric oxygen into ozone. A Geissler tube was exhausted and oxygen was passed into it until the pressure registered several centimeters. The tube was then partially immersed in liquid air and subjected to the discharge from an induction coil. As ozone formed it was condensed owing to the low tem-

[12] Electrochem. and Met. Industry 1906, *4*, 435.
[13] Compt. rend. 1908, *146*, 977; J. Chem. Soc. 1908, *94*, *ii*, 578.
[14] Compt. rend. 1913, *156*, 782.
[15] Ann. Physik. 1909 (iv), *30*, 602.
[16] Physikal. Zeitsch. 1912, *13*, 729.
[17] Ber. 1903, *36*, 3042.

perature, and by repeated treatment in this manner, oxygen was entirely converted into ozone, which was obtained as a dark blue liquid. Goldstein notes that Lenard [18] had observed that ozone was formed by the action on air of sparks from a Leyden jar. The formation of ozone in greatly rarefied air by the method employed by Goldstein was first reported by the latter. Bordier and Nogier [19] could not find that ozone was produced from the oxygen of the air by action of ultraviolet, although others had observed its formation. Using a quartz mercury lamp as the source of the ultraviolet rays, Aubel [20] definitely proved that ozone is produced. Instead of using water to absorb the ozone, olive oil and light petroleum were employed in the first experiments, being placed in porcelain dishes inside a large glass globe surrounding the quartz tube. After several hours' exposure starch iodide showed the presence of ozone in these liquids. When distilled water was submitted to the action of the ultraviolet for fourteen hours, the presence of ozone was detected by its action on a photographic plate. Starch iodide paper was turned blue in two minutes, except where it was covered with a piece of quartz, and thus prevented from coming into direct contact with the ozonized air. In the experiments where water was used to absorb the ozone produced, the resulting solution contained hydrogen peroxide. The presence of hydrogen peroxide in the water is claimed to prove the formation of ozone in the air by the action of the ultraviolet rays. According to Bancroft [21] hydrogen peroxide is formed by the action of bright sunlight or the silent discharge on water and air. Ozone is produced by light of wave-lengths less than 300 μμ (3000 Å) but is decomposed by light of longer wave-lengths. For a given initial quantity of oxygen at a given pressure and temperature, the equilibrium percentage of ozone is fixed if these are the only variables; [22] it is not fixed, however, if ultraviolet radiation is introduced as an independent variable.

A considerable yield of ozone by the action of ultraviolet rays on partially dried oxygen was obtained by Chapman, Chadwick and Ramsbottom.[23] In making observations on the change in volume of the oxygen on exposure to the rays, it was found that a mercury manometer could be used to estimate the pressure, provided that the manometer was connected with the quartz vessel by a sufficient length of capillary glass tubing. Coehn and Sieper were unable to reproduce the results of Chapman in which it is shown that the presence of carbon monoxide increases the amount of ozone produced when oxygen is submitted to ultraviolet. Carbon dioxide is also shown by them to have no effect on the amount of ozone produced.

The production of ozone by ultraviolet rays as practiced by Potter [24] involves the use of a quartz mercury lamp, enclosed by a double walled

[18] Drudes Ann. d. Physik. 1900, *1*, 486.
[19] Compt. rend. 1908, *147*, 354.
[20] Compt. rend. 1909, *149*, 983; 1910, *150*, 96.
[21] J. Physical. Chem. 1912, *16*, 556; J. Chem. Soc. 1912, *102, ii*, 1021.
[22] J. Phys. Chem. 1906, *10*, 721.
[23] J. Chem. Soc. 1907, *91*, 947.
[24] U. S. Patent 854,965, May 28, 1907.

jacket. A current of air is passed through the inner annular space next to the lamp, while water is supplied to the outer space for cooling purposes. The inner wall of the jacket is of silver, glass or other reflecting material which will serve to protect the operator from any ill effects of the rays. By the evaporation of liquid ozone, a gas containing a high percentage of ozone is obtained. Sterilizing apparatus used by Jaubert [25] consists of a horizontal quartz mercury-vapor lamp surrounded by a jacket. The liquid to be sterilized is caused to circulate through the space between the lamp and the jacket. The liquid should contain air or oxygen in solution or suspension, so that ozone is formed when the liquid is subjected to the ultraviolet rays emitted by the lamp.

Davis [26] subjects air to violet and ultraviolet rays and partially ozonizes it between a thin silica plate supported on an iron plate, and a glass disc, having an overlying layer of carbon. The iron and carbon plates are connected to terminals of an electric circuit and air is drawn between the plates by a fan. Spacing blocks of insulating material separate the silica and glass plates. An alternating current is preferred as it is stated to cause the impurities in the air to separate and collect upon the surfaces of the plates.

Fischer and Braehmer [27] devised a form of mercury arc lamp containing a double walled quartz vessel through the annulus of which a gas can be passed, and thus be exposed to the radiation of the arc. The lamp can be immersed in water and its outer glass casing kept cool, and a stream of water (or other cooling liquid) can be passed through the interior of the quartz tube, cooling one coating of the annulus, and hence, as the annular space is only about a millimeter across, cooling the contained gas very considerably. Through this apparatus pure oxygen generated electrolytically from dilute sulfuric acid, was passed and exposed to the radiation from the arc. The results showed that without any cooling, when the temperature rose to 270° C., no ozone was formed. Cooling the gas by water or increasing its speed while maintaining the temperature constant at 15° C. increased the yield of ozone. With constant flow of cooling water, by increasing the current through the lamp from 2 to 6½ amperes, the yield was increased, but further rise of current diminished it, no doubt because of the rise of temperature which it caused. Increase of the oxygen stream corresponding to a rise from 2 to 4 amperes in the generating vessel nearly doubled the yield of ozone, but slightly decreased the percentage in the issuing gas. The experiments indicate that the conversion of oxygen into ozone by ultraviolet is opposed by the decomposition of ozone into oxygen, the speed of which reaction increases rapidly with rise of temperature. These experiments support the view that the production of ozone in the Siemens tube is due to the influence of ultraviolet radiation.

The various methods by which ozone can be prepared and the

[25] French Patent 415,574, July 19, 1909.
[26] U. S. Patent 1,209,132, Dec. 19, 1916; Chem. Abs. 1917, *11*, 549.
[27] Ber. 1905, *38*, 2633.

probable mechanism in the light of the radiation hypothesis are discussed by Rideal and Kunz.[28] The conclusion is drawn that molecular species of one kind can be activated by radiation to different extents. The formation of ozone from dry oxygen in a corona discharge at 16,500 volts between a brass tube and a platinum wire was studied. The distribution of ozone in the discharge was observed by the analysis of the gas mixture drawn from various portions of the discharge, and by the determination of the ratio of intensity of the entrant and emergent beams of ultraviolet passed through the tube. The distribution of ozone in the positive direct current corona differs markedly from that in the negative corona, the ratio of ultraviolet to visible light in each case being large.[29]

Warburg and Regener [30] refer to the silent discharge as possessing both ozonizing and de-ozonizing action and to experiments made to measure these actions in the case of radiations of short wave-length obtained from a spark discharge. As the de-ozonizing action is but little reduced when the discharge occurs in a thin-walled glass tube these investigators conclude that the wave-length of the active rays is under 300 μμ (3000 Å). The formation of ozone by the silent discharge, it is claimed by Kruger and Moeller,[31] cannot be due to electrolytic action, and it is suggested that the liberation of secondary rays by the action of high speed cathode rays on the oxygen molecules is the determining factor in the formation of ozone.[32]

Lenard [33] has shown that ozonizing action is due to light of short wave-length, less than 200 μμ (2000 Å). Regener [34] proved that there is also a de-ozonizing action for wave-lengths between 300 μμ (3000 Å) (absorption by glass) and 185 μμ (1850 Å) (absorption by quartz). This is in agreement with the fact that ozone shows a strong maximum absorption for rays of wave-length 257 μμ (2570 Å). When using gaseous ozone in small concentrations Ledanburg and Lehmann [35] found the absorption reached to about 316 μμ (3160 Å) in the ultraviolet, but as the concentration increased, new bands appeared and extended into the region of longer wave-length. Liquid ozone did not show any absorption bands in the visible spectrum and there were

[28] J. Phys. Chem. 1920, *24*, 379; Chem. Abs. 1920, *14*, 2578.

[29] Filtration of ultraviolet rays is resorted to by Cornelius, Chim. et. Ind. 1921, *6*, 218; German Patent 318,065, 1916, to eliminate the rays forming detrimental quantities of ozone.

[30] Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1228; J. Chem. Soc. 1904, *86*, ii, 692.

[31] Festschrift. W. Nernst. 1912, 240; J. Chem. Soc. 1912, *102*, ii, 1126.

[32] For industrial purposes, Jobling, Martin's Industrial Gases, N. Y., 1916, 134, states the only practical method of producing ozone is that of passing dry air through a chamber where it can be subjected to the influence of a silent high-tension electric discharge. It is not certain whether the production of ozone by silent discharge is fundamentally an electrolytic phenomenon, dependent upon the electric stress developed, or whether it is to be attributed to the ultraviolet rays developed. The latter is the more probable.

[33] Ann. der Physik. 1900, *1*, 486.

[34] Ann. der Physik. 1906, *20*, 1033.

[35] Chem. Centr. 1906, i, 1727; Ber. Deut. phys. Ges. 4, 125.

no bands in the ultraviolet. Dewar [36] has demonstrated by means of the iodine starch paper test that ozone is formed when light falls on liquid oxygen.

Bahr [37] exposed ozonized oxygen to ultraviolet rays from a quartz-mercury lamp and measured the rate at which the ozone was decomposed. The rate of decomposition increases rapidly as the pressure on the gas is reduced. For a given intensity of the incident ultraviolet radiation, the ozone disappears at a rate which agrees with the requirements of the equation for a unimolecular change, if the pressure is kept constant. The rate of decomposition of ozone in ultraviolet has also been investigated by Weigert.[38] The results with freshly prepared mixtures of oxygen and ozone are reproducible with an accuracy of about 30 per cent. The observed rate of decomposition is the sum of the spontaneous decomposition which also takes place in the dark, and the reaction under the influence of radiation. The order of the light reaction is approximately unimolecular. Alternate illumination and periods of darkness eliminate certain sources of error. In order to investigate the photochemical reaction of ozone it was necessary to use a part of the spectrum where ozonization of oxygen does not occur. This is obtained by Weigert [39] by using a quartz-mercury lamp, and allowing the rays to pass through a layer of air before entering the reaction vessel. No trace of hydrogen peroxide is formed, and there is only an extremely slow reaction in the dark. In ultraviolet rays, however, about one-third of the ozone originally present disappears in two minutes. The total amount of ozone decomposed is proportional to the ozone concentration, while the amount of hydrogen oxidized approaches an upper limit, which is proportional to the concentration of the hydrogen. The above results indicate that in the activation of oxygen by ultraviolet rays two photochemical reactions occur. In the formation of water from hydrogen and oxygen, the oxygen is first ozonized by the short rays, and then reacts with hydrogen under the influence of the long rays.

Weigert and Böhm [40] have made a quantitative investigation of the catalytic influence of ultraviolet rays on the simultaneously occurring ozone decomposition and the water formation, when this radiation is allowed to act on mixtures of hydrogen and ozonized oxygen. The formation of hydrogen peroxide was not observed.

Ozone has also been found to be decomposed by visible light. By the use of light filters, Griffith and Shutt [41] observed that the effective regions of the spectrum lie between 760 to 670 μμ (7600-6700 Å) and 615 to 510 μμ (6150-5100 Å). The same workers have investigated the effect of visible light on mixtures of ozone and other gases.[42] Mixtures of ozone and oxygen and of ozone, oxygen and hydrogen

[36] Engineering 1910, *89*, 116.
[37] Ann. Physik. 1910, *33*, iv, 598; J. Chem. Soc. 1910, *98*, ii, 949.
[38] Zeitsch. physikal. Chem. 1912, *80*, 78; J. Chem. Soc. 1912, *102*, ii, 715.
[39] Ber. 1913, *46*, 815.
[40] Z. Physik. Chem. *90*, 189; Chem. Abs. 1915, *9*, 3013.
[41] J. Chem. Soc. 1921, *119*, 1948.
[42] J. Chem. Soc. 1923, *123*, 2752.

were subjected to rays of wave-length 360 to 760 μμ (3600 to 7600 Å), and of constant intensity. In the first case the velocity of the reaction $2O_3 \longrightarrow 3O_2$ is proportional to the square of the ozone concentration. In the second case the same reaction takes place and also the reaction, $H_2 + O_3 \longrightarrow H_2O + O_2$. Hydrogen has a strong catalytic effect on the first reaction. The extent of the second reaction is small, but it becomes predominant when the ozone concentration is below 2.4 per cent. With mixtures of ozonized oxygen and carbon monoxide, two reactions occur, (a) $2O_3 \longrightarrow 3O_2$, (b) $O_3 + CO \longrightarrow CO_2 + O_2$.[43] In the presence of other gases only the first reaction occurs. In mixtures of ozonized oxygen and carbon monoxide containing from 1.6 to 8 per cent of ozone, the fraction of ozone forming carbon dioxide varies in an irregular manner between 0.06 and 0.01. In mixtures low in ozone, hydrogen reacts to a greater extent with ozone photochemically activated than does carbon monoxide under similar conditions. The gases investigated catalyze reaction (a) in the order—hydrogen, helium, argon, nitrogen, carbon monoxide and carbon dioxide, the effect of hydrogen far exceeding that of the others. Helium, argon, and nitrogen produce a definitely stronger effect than carbon monoxide or carbon dioxide.

The decomposition of ozone by light in presence of chlorine has been studied quantitatively by Weigert,[44] the rays of a quartz mercury lamp being used, and the rate of decomposition being measured by means of the change of pressure of the gas. There is no induction period, and decomposition stops when the gas is cut off. The rate of decomposition is independent of the concentration of the chlorine and it is nearly proportional to the intensity of the light. By placing a vessel containing chlorine between the source of light and the ozone tube, a measurement of the quantity of light absorbed by the chlorine is obtained. In this way Weigert showed that the rate of decomposition of the ozone is proportional to the quantity of light absorbed by the chlorine mixed with it. It is suggested that the light produces some intermediate product which is destroyed rapidly by the action of ozone.

An attempt to activate chlorine photochemically has been made by Wendt[45] along the same general lines by which he succeeded in preparing activated forms of nitrogen and hydrogen using the brush electric discharge, but he was unsuccessful. The next step was to set up an apparatus consisting essentially of an ultraviolet lamp in a central glass tube surrounded by a second glass tube to form an annular space through which dry chlorine was passed and subsequently conducted into the dark, where it was mixed through a three-way cock with hydrogen. Tests of the mixed gases showed that no hydrochloric acid was formed. In other words the chlorine was not activated. The two gases were inert compared to those reported in Draper's experiments in which rapid combination is secured by exposing the mixture to light.

[43] J. Chem. Soc. 1923, *123*, 2767.

[44] Zeitsch. Elektrochem. 1908, *14*, 591.

[45] Chem. & Met. Eng. 1921, *24*, 83. For photodecomposition of chlorine water and hypochlorous acid solutions, see Allmand, Cunliffe and Maddison, J. Chem. Soc. 1925, *127*, 822.

Wendt, Landauer and Ewing [46] find that irradiation of chlorine by a 2000-watt mercury lamp or by a high-potential electric discharge is incapable of converting it into a form such that it will react with hydrogen in the dark. That chlorine after isolation may be brought to react with hydrogen in the dark is due to the destruction of substances which inhibit the reaction, rather than to any activation of the chlorine. On the other hand, it is claimed by Venkataramaiah [47] that pure chlorine, prepared by heating gold chloride, and activated by the silent electric discharge, by electrical discharge at 20 mm. pressure, by ultraviolet rays, or thermally, combines with ozone to form chlorine monoxide, with sulfur to form sulfur monochloride, with tellurium to form tellurium dichloride, and with benzene in the dark to form benzene hexachloride. It does not react with carbon, and is unstable about 50°. The activation of chlorine is accompanied by a contraction in volume, indicating that the activity is probably due to the presence of complex molecules. Likewise,[48] it has been noted that if chlorine gas is subjected to the silent electric discharge in a manner similar to that used in the preparation of ozone, a chemically active form of chlorine is obtained. The activity of this element is even greater than if subjected to the silent electric discharge and ultraviolet simultaneously. It has been supposed that under the influence of the electric discharge the chlorine forms a body analogous to ozone. It is, therefore, thought that the activity of the chlorine treated in this way depends simply on impurities such as air and water, as a result of which ozone or unstable chlorine oxide is formed.

The absorption of light by chlorine between 254 μμ and 643 μμ (2540 Å and 6430 Å) has been determined by Halban and Siedentopt [49] for nineteen wave-lengths using lines of mercury, zinc and cadmium and between 383 μμ and 451 μμ (3830 Å and 4510 Å) using a Nitra-lamp for twelve wave-lengths. The method of observation was a photoelectric two-cell arrangement.[50] The results show that within the pressure range investigated (760 mm. and downwards) Beer's law is true. The absorption curve shows a maximum in the ultraviolet at about 334 μμ (3340 Å) and a minimum in the yellow. From yellow to red, the absorption again increases, and reaches a maximum which probably lies between 614 μμ and 643 μμ (6140 and 6430 Å). No difference could be observed between the absorption of dry and moist chlorine.

Trautz [51] has calculated the velocity coefficients of a number of gas reactions and in connection with these calculations the specific heat of chlorine at constant pressure has been measured, and the ratio of the specific heats at constant volume and at constant pressure determined by Kundt's method. It is shown by two different methods that the constant volume diminishes to some extent when the gas is exposed

[46] J. Am. Chem. Soc. 1922, *44*, 2377.
[47] J. Phys. Chem. 1923, *27*, 74.
[48] Handbuch der Biochem. Arbeitsmethoden IV, 870.
[49] Z. physikal. Chem. 1922, *103*, 71; J. Chem. Soc. 1923, *124*, *ii*, 48.
[50] J. Chem. Soc. 1922, *122*, *ii*, 332.
[51] Zeitsch. Elektrochem. 1912, *18*, 513; J. Chem. Soc. 1912, *102*, *ii*, 746.

to the rays of a quartz lamp. According to the first method it is found that the wave-length in the Kundt's tube alters on exposing the gas to light, while according to the alternative method, the expansion is not the same when the same amount of heat is supplied to the illuminated and non-illuminated gas under conditions otherwise similar.

Radel [52] has investigated the reaction between chlorine and water vapor by the ultra-microscopic method of observation. It was found that when moist chlorine was illuminated there was formed, after an induction period which varied between one hundredth and thirty seconds, a fine cloud of single drops which grew rapidly in size. On screening off the illumination the particles decreased in size and finally disappeared. The same effect was observed when the chlorine was previously ionized. Radiation of the reaction mixture with polonium and with radium bromide produced the same effect, although this was considerably weaker than that produced by light.

The temperature coefficient of the photochemical action of monochromatic light on a mixture of chlorine and hydrogen has been considered by Padoa and Butironi.[53] The results of experiments on the variability of the temperature coefficient of the reaction velocity of photochemical processes with changes in the wave-length of the light used, have made desirable a similar study of simple photochemical reactions in which there can be no doubt that the reaction is purely photochemical. The reaction of hydrogen and chlorine in the presence of light fulfills these requirements. Favre and Silbermann [54] found that different parts of the spectrum produced a catalysis of varying intensity. Bunsen and Roscoe found a maximum intensity of action between 413 and 395 μμ (4130 and 3950 Å).[55] They devised an actinometer for the study of this reaction, a modified form of which was used by Padoa. It was so constructed that the gas bulb could be kept in a thermostat with glass walls. The apparatus was mounted in a camera obscura and the source of light at one side was in a box provided with a hole, through which the beam to be studied was admitted to the bulb. Ultraviolet radiation was obtained from a mercury lamp. It was observed that the acceleration produced by increases of temperature is small for the ultraviolet, is greater for violet and blue light and is maximum for green; for white light it is intermediate. The temperature coefficients when calculated bring this out still better, for white the coefficient is 1.29; for green 550-530 μμ (5500-5300 Å) 1.50; for blue 490-470 μμ (4900-4700 Å) 1.31; for violet 460-440 μμ (4600-4400 Å) 1.21; for ultraviolet 400-350 μμ (4000-3500 Å) 1.17.

Berthelot and Gaudechon [56] have made a study of the stability of the hydrogen compounds with the chlorine and oxygen groups of elements towards light of different wave-length. As in the case of decomposition by heat, it holds good that, in the same family of elements,

[52] Z. Physik. Chem. 1920, *95*, 378; Chem. Abs. 1920, *14*, 3369.
[53] Chem. Abs. 1917, *11*, 1356; Att. accad. Lincei. 1916, *24*, II, 215.
[54] Ann. chim. phys. *3*, 37, 297.
[55] Bevan's experiments, Proc. Camb. Phil. Soc. *12*, 398, showed that the temperature influences the velocity of this reaction and Kastle and Beatty, Am. Chem. J. *20*, 159, found that at 120° the velocity of reaction is zero.
[56] Compt. rend. 1913, *156*, 889; J. Chem. Soc. 1913, *104*, ii, 369.

the stability of the hydrogen compounds with respect to light decreases as the atomic weight increases. Substances which are only dissociated at high temperatures are similarly only affected by the very rapid vibrations of the extreme ultraviolet. Hydrogen chloride requires ultraviolet $\lambda < 200$ $\mu\mu$ (2000 Å) for decomposition, which even then is slow, while under similar conditions hydrogen bromide is rapidly and completely decomposed. Hydrogen iodide is decomposed by blue and violet light. A similar relationship is found in the case of water vapor, hydrogen sulfide, selenide and telluride.

Thiele [57] reports that in ultraviolet rays interaction takes place in a mixture of hydrogen chloride and air, even when the gases are dried by means of sulfuric acid. Hydrobromic acid is also decomposed by air in ultraviolet.[58]

The influence of light on the gaseous systems hydriodic acid, hydrobromic acid, hydrochloric acid, and their components has been investigated by Coehn and Stuckardt [59] from both sides of the equilibrium, at room temperature. The experiments have been carried out in quartz glass, uviol glass, and Jena glass, which permitted the determinations of the photochemical equilibrium in three different spectral regions. The percentage decomposition of the acid when equilibrium is attained is given below:

Acid	In Quartz Glass 220 μ.	In Uviol Glass 254 μ.	In Jena Glass 300 μ.
Hydriodic	92.2	100	100
Hydrobromic	100	about 20	0
Hydrochloric	0.42	0	0

The absorption of the halogen acids and the halogens in the ultraviolet has been studied, and it has been found that it depends upon the thickness of the absorbing layer. Various conclusions regarding the position of the photochemical equilibrium in the different spectral regions are drawn from a consideration of the course of the absorption curves with increasing thickness of the absorbing layer.

The equilibrium point of hydrogen chloride in the dark lies practically at the point of complete formation of this compound from its elements. This equilibrium can be brought about in the absence of light by submitting the mixture of hydrogen and chlorine to the catalytic action of charcoal. Coehn and Wassiljewa [60] find that if pure hydrogen chloride is submitted to the action of ultraviolet rays from a quartz mercury lamp, it is split up to such an extent that, on collecting the gases over a solution of potassium iodide, about 2 cubic centimeters of hydrogen are produced in a quarter of an hour. The hydrogen chloride was passed through a quartz tube, which was at a distance of about 2 centimeters from the lamp, the tubing through which the gases were led

[57] Z. angew. Chem. 1909, *22*, 2472.

[58] On the photochemical formation of hydrogen bromide in a silica vessel illuminated by a tungsten arc lamp see Bodenstein and Lutkemeyer, Z. physikal. Chem. 1924, *114*, 208; J. Chem. Soc. 1925, ii, 218.

[59] Z. physik. Chem. 1916, *91*, *722*; Chem. Abs. 1917, *11*, 749.

[60] Ber. 1909, *42*, 3183.

away from the quartz tube being protected from all light. When the quartz tube was replaced by one made of ordinary glass, or of uviol glass, no decomposition of the hydrogen chloride took place.

The minimum aqueous vapor pressure observed by Coehn and Jung [61] necessary for the photochemical combination of hydrogen and chlorine on exposure to rays corresponding to the visible spectrum was found to lie between 10^{-7} and 10^{-5} millimeters of mercury. The maximum wave length inducing photochemical combination is less than 300 μμ (3000 Å) in perfectly dry gas mixtures and 540 μμ (5400 Å) in the case of moist gases.

Some details of the work of Chapman, Chadwick and Ramsbottom [62] show that after long exposure with intermittent illumination dry carbon dioxide at atmospheric pressure was decomposed to an extent from 2.6 to 3 per cent. The amount of decomposition was in each case estimated by the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonized. When the moist carbon dioxide was submitted to the action of ultraviolet, no increase of pressure within the apparatus could be observed, and no carbon monoxide could be detected in the gases withdrawn after the experiment. Carbon dioxide nearly saturated with water vapor was admitted to the apparatus until the pressure was equal to that of the atmosphere. Gas was then withdrawn until the manometer indicated that the pressure within the apparatus was 30 mm. The pressure did not increase when the gas was submitted to the action of ultraviolet rays, and the gas withdrawn at the end of the experiment did not contain either carbon monoxide or oxygen. When alkaline pyrogallol was added, a slight change in its color was noted, but no decrease in the volume of the gas could be detected. Carefully dried carbon dioxide at a pressure of 36 mm. was next submitted to the action of the intermittent light for forty-five hours. The analysis of the gases withdrawn at the end of the experiment showed that 46 per cent of the carbon dioxide had been decomposed.

The above experiments demonstrate that dry carbon dioxide is decomposed by ultraviolet radiation, the percentage decomposition being increased by a reduction of pressure, but that under the same conditions the moist gas at all pressures remains practically unchanged. Now it is well known that in a balanced reaction in a system kept at the same temperature as its surroundings the state of equilibrium is unaffected by a small amount of a catalyst. The extent, for example, to which carbon dioxide is decomposed when it is maintained at constant temperature in an opaque vessel is dependent only on the temperature and the pressure, and is independent of the degree of desiccation. The reason for this well-established fact is that the distribution of energy among the various groups of molecules after equilibrium has been established is unaffected by the presence of a small amount of a foreign substance. When, on the other hand, the reaction is photochemical, the position of equilibrium is not independent of the catalyst, as the above

[61] Z. physikal. Chem. 1924, *110*, 705.
[62] J. Chem. Soc. 1907, *91*, 942; see also J. Chem. Soc. 1906, *89*, 22.

experiments demonstrate, and this fact leads to the conclusion that under such conditions the catalyst (moisture) exerts a marked influence in determining the mode of distribution of the energy among the molecules of the reacting substances (the two oxides of carbon and oxygen).

The action of ultraviolet rays on carbon dioxide has been determined at various pressures by Coehn and Sieper.[63] It is shown that an unchangeable stationary condition is set up with the time on exposing carbon dioxide to ultraviolet. The wave-length of the active rays lies below 254 μμ (2540 Å). The decomposition is modified with increasing pressure more than is demanded by the law of mass action, as is also the case in the photochemical decomposition of water vapor. The decomposition is inversely proportional to the pressure. These investigators also find that the photochemical decomposition of carbon dioxide is very sensitive to traces of water vapor, but in the opposite sense to all other photochemical reactions. For example, in the case where a dry gas is decomposed to the extent of 18 per cent, the merest trace of moisture reduced the amount of decomposition to 0.1 per cent, and neither formic acid nor formaldehyde is formed, and the water undergoes no change. On the other hand it is shown that on irradiating a mixture of equal volumes of carbon dioxide and hydrogen with ultraviolet, formaldehyde is produced.

The reduction of carbon dioxide in *aqueous solution* by very finely divided hydrogen steadily diminishes in velocity with the time according to Zenghelis.[64] It takes place very slowly in the dark, but is markedly accelerated by sunlight and still more so by ultraviolet rays. In all cases the formaldehyde first produced undergoes polymerization.[65]

The combination of carbon monoxide with oxygen in ultraviolet rays is found by Herchefinkel [66] to be reversible, considerable quantities of carbon monoxide being formed when dry carbon dioxide is exposed in quartz vessels, in the presence of mercury, to this radiation. He confirms Cameron and Ramsay's observation that the decomposition is also effected by radium emanation.[67]

Coehn and Tramm [68] have examined the influence of pressure and degree of desiccation on the explosibility of mixtures of carbon monoxide and oxygen and have shown that a moist mixture can be exploded by a spark at any pressure, that a mixture dried by short exposure to the action of solid carbon dioxide and alcohol cannot be exploded but ignites and burns quietly, and that a mixture which has been cooled for a sufficient time cannot be ignited but in the latter case a pale bluish zone forms round the spark gap and slight combination is indicated by a small diminution in pressure. Exposure to mixtures belonging to the three types to ultraviolet rays from a quartz mercury vapor lamp

[63] Z. physik. Chem. 1916, 347; J. Chem. Soc. 1916, *110*, 281; Chem. Abs. 1916, *10*, 2549.

[64] Compt. rend. 1920, *171*, 167; J. S. C. I. 1920, *39*, 596 A.

[65] For further discussion of the reactions of carbon dioxide and of formaldehyde in ultraviolet light see Chapter 11, Photosynthesis.

[66] Compt. rend. 1909, *149*, 395.

[67] J. Chem. Soc. 1908, *93*, 981.

[68] Ber. 1921, *54*, 1148.

leads to practically the same result in each case, combination occurring to the extent of 4 or 5 per cent within an hour. The presence of moisture, therefore, is considered not to play a part in the union of carbon monoxide and oxygen under the influence of radiant energy. It is noted by Thiele [69] that carbon monoxide and oxygen when exposed to ultraviolet unite less readily than hydrogen and oxygen.

Berthelot and Gaudechon [70] have shown the aptitude of carbon monoxide to form additive products by its behavior towards certain gases under the influence of ultraviolet rays. In the presence of nitric oxide a small proportion of the carbon monoxide is oxidized by the oxygen set free from the decomposition of the nitric oxide. With water the reaction is more complex, one part of the carbon monoxide combining directly with the water, yielding formic acid, while the rest combines with the hydrogen and oxygen, resulting from the dissociation of the water to give formaldehyde and carbon dioxide respectively. Of the halogens, chlorine combines with carbon monoxide but bromine and iodine are without action.

The photochemical formation of phosgene has been studied by Bodenstein.[71] The chlorine used contained 0.08 per cent oxygen and a trace of water. Carbon monoxide was made by the reaction of sulfuric acid and formic acid, and was freed from oxygen, carbon dioxide and water. The results with various mixtures of carbon monoxide and chlorine are very complicated, and are influenced by the moisture present. Experiments on the relation between the radiations absorbed and the amount of material transformed show that oxygen retards the reaction and exercises a rather constant effect until just at the end, when its effect is suddenly diminished. Oxygen is sensitized by irradiated chlorine. Carbon dioxide formation is, other things being equal, proportional to the carbon monoxide pressure, increases with the chlorine pressure, but more slowly than directly proportional to it, and decreases with increasing oxygen concentration, but not so rapidly as to be inversely proportional to it. The sensitized reaction also shows a large Draper effect.

Coehn and Becker [72] find that when carbonyl chloride is passed through a quartz tube at the ordinary temperature, and at the same time submitted to the action of rays from a quartz mercury lamp, it is partly decomposed into carbon monoxide and chlorine. When 1 c.c. of carbonyl chloride is passed through the quartz tube (20 centimeters long and 0.5 centimeters in diameter) per minute, the amount of decomposition is 3.3-4 per cent. The effect is chiefly due to the short ultraviolet rays, since the use of tubes of uviol glass, which are transparent only to waves of greater wave-length than 265 μμ (2650 Å) resulted in a degree of decomposition of only 0.46-0.5 per cent. In ordinary glass tubes there was no decomposition. Coehn and Becker remark that in all the cases hitherto examined, namely, the photochemical equilibria of sulfur

[69] Z. angew. Chem. 1909, *22*, 2472.
[70] Compt. rend. 1913, *157*, 129.
[71] Rec. trav. chim. 1922, *41*, 585; Chem. Abs. 1923, *17*, 687.
[72] Ber. 1910, *43*, 130.

trioxide, hydrogen chloride, and carbonyl chloride, the actual equilibrium is affected only by ultraviolet rays. Rays of greater wave-length simply act catalytically on the attainment equilibrium. Wherly [73] reports that while experiments using ultraviolet for the production of phosgene by the union of carbon dioxide and chlorine have been successfully tried, the disadvantages on a commercial scale are manifest. By far the greater proportion of phosgene is manufactured by passing carbon monoxide and chlorine over platinized asbestos, charcoal or boneblack heated to redness.

Exposure of mixtures of carbonyl chloride and hydrogen to ultraviolet radiation results in the 97 per cent decomposition of the carbonyl chloride according to the scheme $COCl_2 \rightarrow CO + Cl_2$, followed by $Cl_2 + H_2 \rightarrow 2HCl$. In the absence of hydrogen, the equilibrium mixture under similar conditions contains about 4 per cent of carbon monoxide and chlorine. Bredig and Goldberger [73a] hoped to obtain formaldehyde according to the scheme $COCl_2 + 2H_2 \rightarrow CH_2O + 2HCl$. At 10°, minute traces of this substance were obtained and none at all at 80°. The walls of the reaction vessel were observed to be coated with a white to brown deposit. The photolysis of pure gaseous formaldehyde was therefore studied at 80° and 195°. Carbon monoxide and hydrogen were the chief decomposition products. Small amounts of methane and carbon dioxide were observed and at the higher temperature a sugary substance was formed on the walls. The decomposition cannot apparently be represented by any simple stoicheiometric expression. At 80°, the decomposition follows the unimolecular law but at 195°, and for high concentrations of vapor, all the rays are absorbed and the rate of reaction is independent of concentration. The failure to obtain formaldehyde from carbonyl chloride is explained on the assumption that on formation it undergoes a polymerization to solid products and also suffers a photochemical decomposition.

Humiston [74] passed a mixture of carbon monoxide and fluorine through a quartz tube while exposing it to the action of ultraviolet rays, but no products were obtained that could be determined even by condensation at — 80°, hence it is concluded that no reaction occurred.

The reaction $SO_2 + Cl_2 = SO_2Cl_2$ in the dark cannot be considered as a pure gaseous reaction. Only on the addition of animal charcoal as a catalyzer were easily reproducible velocity measurements obtained; then both reactions proceeded as absorption processes in which the velocity of diffusion did not appreciably interfere. In both cases the reaction is approximately normal, though more so in the decomposition than in the formation of the oxychloride. In the latter case the reaction constants decreased more rapidly, corresponding to a lower order of reaction (absorption). The temperature coefficient of formation is about 1, that of the decomposition about 1.5, though both values are too small on account of the slower temperature effect of absorption. The formation of the oxychloride from sulfur dioxide and chlorine in glass

[73] Color Trade Journal 1918, 8.
[73a] Z. physikal Chem., 1924, *110*, 521.
[74] J. Phys. Chem. 1919, *23*, 572; Chem. Abs. 1920, *14*, 534.

vessels under the radiation of a quartz lamp at 291° and at various concentrations has been studied by Trautz.[75] The reaction especially at the higher temperature proceeds smoothly as a second order reaction; the constants at the higher temperature are without variation. By irradiation, sulfuric oxychloride is not the only product of the reaction; if the relatively small periods of exposure are separated by several hours of darkness, other substances are formed which cause a decrease in the velocity constant of the reaction. When continuous irradiation was employed, constants were no longer obtained, probably on account of the other products of the reaction. A temperature increase of 80° decreased the velocity of formation corresponding to a temperature coefficient of 0.88 for each 10°. The velocity of the formation-reaction is of the same order as that which is catalyzed by animal charcoal in the dark, whether uviol light or that from a quartz lamp is used. The formation of sulfuric oxybromide from sulfur dioxide and bromide in the light of a Nernst lamp or in the dark, between 106° and 202° in glass vessels without a catalyzer, could not be accomplished. But carbon oxybromide could be readily formed from carbon monoxide and bromine vapor, an equilibrium being quickly reached which corresponded to a very large dissociation of the carbon oxybromide. From the equilibrium constants at 73° and 181° the heat of formation was calculated as about 3,000 cal.

When 2.38 cubic centimeters of sulfur dioxide were irradiated over mercury for three hours a contraction of 0.18 cubic centimeters was observed[76] and the mercury became encrusted with a sulfate, sulfur being deposited on the sides of the tube. A mixture of sulfur dioxide and oxygen behaved in the same way, sulfur being deposited, although oxygen remained in excess.

Hill[77] reports that the decomposition of gaseous sulfur dioxide, under the influence of light from a uviol mercury vapor lamp takes place according to the equation

$$3\,SO_2 \rightarrow 2\,SO_3 + S.$$

By interposing various filters it was found that the chief response is at 313 μμ (3130 Å), lying within the first absorption band of sulfur dioxide. Shorter wave-lengths are ineffective because of their low intensity. Considering the thermal union of sulfur and oxygen from the standpoint of critical increments, it is necessary, in order to get agreement, to conclude that oxygen reacts with molecular sulfur rather than with the atom.

Coehn and Becker[78] have studied the formation of sulfur trioxide from sulfur dioxide and oxygen under the influence of the radiation from a quartz mercury lamp. Experiments made with a quartz reaction vessel mounted within a mercury lamp showed that the formation of

[75] Z. Elektrochem. 1915, *21*, 329; Chem. Abs. 1915, *9*, 3008.
[76] Berthelot and Gaudechon 1910, *150*, 1517; J. Chem. Soc. 1910, *98*, *ii*, 606.
[77] Tr. Far. Soc. 1924, *20*, 107; Chem. Abs. 1924, *18*, 1950; J. Chem. Soc. 1925, *128*, *ii*, 56.
[78] Z. physik. Chem. 1910, *70*, 88.

sulfur trioxide proceeds fairly rapidly even at the ordinary temperature and more rapidly at higher temperatures. The equilibrium is quite distinct from that attained in daylight. With a mixture of one part sulfur dioxide to one of oxygen, equilibrium is attained with a production of 65 per cent of sulfur trioxide. This equilibrium can also be attained starting from sulfur trioxide. At 160° C. with the gases confined in the reaction chamber equilibrium was attained in one hour. In daylight at temperatures below 450° C. the equilibrium condition corresponds to practically 100 per cent of sulfur trioxide. Again the irradiation equilibrium (attained on exposure to the radiation from the mercury lamp) is not displaced by rise of temperature up to 800° C., whereas the dark equilibrium is displaced considerably by rise of temperature above 450° C. With a mixture in the proportions of one part of sulfur dioxide to thirteen parts of oxygen, at 800° C., the yield of sulfur trioxide is 80 per cent on exposure to the rays from the mercury lamp, whereas in daylight the yield is 44 per cent of sulfur trioxide. The temperature coefficient of the velocity of the photochemical reaction was found to be 1.2. Coehn and Becker consider that a technical photo chemical process for the production of sulfuric acid is feasible, since on using air in place of oxygen no oxides of nitrogen are formed. Some experiments were made with a special mercury lamp composed essentially of a quartz tube, 115 cm. long and 1.8 cm. diameter. This was enclosed in a tube of opaque quartz, 100 cm. long and 5 cm. diameter, the annular space between the two serving as reaction chamber. At 450° C., and with the gaseous mixture passing at the rate of 100-150 c.c. per minute, yields of 67.4, 70.8, 92 and 90 per cent respectively of sulfur trioxide were obtained, with 0.78, 0.66, 8.7 and 9.3 molecules of oxygen per molecule of sulfur dioxide.

Sulfuric acid may also be prepared [79] by exposing a mixture of sulfur dioxide and oxygen (or air) preferably containing excess of oxygen, to ultraviolet of low intensity, the gases being heated above 300° C. The yield of sulfur trioxide is increased if the reaction mixture after exposure to the rays be cooled in stages.

The gaseous reaction between hydrogen and sulfur has been investigated by Norrish and Rideal [80] and has been found to be strongly catalyzed by the ultraviolet rays from the mercury vapor lamp, of calculated wave-length. The absorption spectrum of sulfur vapor contains a band with maximum absorption at 275 μμ (2750 Å) in good agreement with the earlier work of Graham.[81] This corresponds with a critical increment of activation, q = 51,670 cal. per g.-atom, in agreement with the value previously found for the critical increment of activation of the (dark) gaseous reaction between hydrogen and sulfur, 51,400 cal., and also with the heat of dissociation of the S_2 molecule, 50,000 cal. Conversely, ultraviolet radiation of wave-length about 270 μμ (2700 Å) is photochemically active in initiating a gaseous reaction between hydrogen and sulfur vapor, proportional to the pressure

[79] German Patent 217,772, July 9, 1907.
[80] J. Chem. Soc. 1924, *125*, 2070; see also ibid. 1923, *123*, 3202.
[81] J. Chem. Soc. 1910, *98*, ii, 1015.

of the sulfur vapor. In the gaseous state, reactions between hydrogen and sulfur can take place only between sulfur atoms, which are produced both by collisions and by photochemical dissociation. In addition, a reaction at the surface takes place between hydrogen and activated S_8 molecules, and is not affected by ultraviolet radiation, the activation being entirely caused by collisions. In all cases, whether the activation takes place in the gaseous state or at the surface, by radiation or by collision, the energy of activation is constant, indicating that, in activation by collisions, the Newtonian laws of inelastic impact do not apply. Instead the process obeys the laws of quantum dynamics, the same amount of energy being extracted from the colliding molecules, whatever the force of their impact, providing this exceeds a certain magnitude. In these reactions, activation of the sulfur molecule, whether S_2 or S_8, is synonymous with the dissociation of one valency "bond."

Coehn and Pringent [82] have endeavored to ascertain whether the decomposition of ammonia by the ultraviolet is complete or whether a determinable amount of ammonia remains undecomposed. Ammonia was sealed up in quartz tubes and exposed to the rays of a quartz mercury lamp, and the gas examined after various periods of exposure. It was found that after one hour ammonia was still present, but after six hours ammonia could not be detected by means of Nessler's reagent, thus showing that the decomposition was complete.[83] Weigert [84] has shown that when a mixture of nitrogen and hydrogen is sensitized by the addition of chlorine, ammonia is formed by ordinary visible light. Coehn and Pringent have passed similar mixtures, dry and damp, through a quartz tube, extending through the center of a quartz mercury lamp, and have been unable to show the formation of ammonia even in such small amounts as would give the reaction with Nessler's reagent.

Berthelot and Gaudechon [85] report that nitrogen and oxygen do not combine under the influence of rays from a quartz mercury lamp. Nitrous and nitric oxides are decomposed into their elements, but in each case a portion of the gas unites with oxygen to form higher oxides. A mixture of nitrous oxide and oxygen behaves in a similar fashion. In studying the impact effects in nitric oxide and nitrogen, Bazzoni and Waldie [86] observed that nitric oxide at low pressures is not broken down by ultraviolet rays or heat radiation, while hot metals produce dissociation and elimination of the oxygen, leaving essentially nitrogen.

Fischer [87] formed a high-tension luminous arc in air at the base of a vertical glass tube five centimeters in diameter and one meter long and obtained brown fumes in the tube, visible when veiled against a

[82] Zeitsch. Elektrochem. 1914, *20*, 275; J. Chem. Soc. 1914, *106*, *ii*, 404.

[83] The decomposition of ammonia by means of a hot platinum wire has been measured by Baly and Duncan, J. Chem. Soc. 1922, *121*, 1008, who find that two types of ammonia may be prepared, an inactive and an active modification, which are decomposed to different extents by the same quantity of energy.

[84] J. Chem. Soc. 1908, *94*, *ii*, 5.

[85] Compt. rend. 1910, *150*, 1517; J. Chem. Soc. 1910, *98*, *ii*, 606.

[86] J. Frank. Inst. 1924, *197*, 56; Chem. Abs. 1924, *18*, 784.

[87] Z. physik. chem. Unterricht 1920, *33*, 64; Chem. Abs. 1920, *14*, 3562.

white background by daylight. By electric incandescent light they do not show well but with a quartz mercury lamp they become visible.

Nitrogen in contact with mercury in a mercury arc is dissociated but not to as great an extent as hydrogen under like conditions.[88] However, above 70 volts a very active form of nitrogen appears, the conductivity of the arc increasing enormously, and a "flare" is produced.

[88] Duffendack and Compton, Phys. Rev. 1924, *23*, 583.

Chapter 7.

Various Photochemical and Photolytic Reactions. General and Inorganic.

Since the time of Berzelius it has been generally recognized that many reactions which do not proceed under the usual conditions may be made to progress in the presence of certain substances, denominated catalysts. As time has passed the number of such reactions reported has increased enormously, and numerous theories have been evolved to explain their mechanism. Likewise it began to be observed that light exerts a profound influence on many chemical reactions, and that the radiations of short wave-length, comprising the ultraviolet region, are particularly active in this respect. Some of the reactions thus brought about may also be effected with ordinary catalysts, while in other cases it has not yet been found possible to carry on the reaction without access of light.[1] The majority of researchers in photochemistry have assumed that the amount of chemical change in a given system effected by light of a specified wave-length is proportional to the light absorbed. Although this is a fundamental principle of the greatest importance, the experimental evidence for its universal validity is not conclusive. Draper [1a] in the case of the photochemical interaction of hydrogen and chlorine, found that the above relation was at least approximately true, but its accuracy has been challenged by Baly and Barker [1b] who observed that the rate of combination of hydrogen and chlorine increases with the intensity of the light more rapidly than Draper's law requires. The results of research by Chapman [1c] seem to demonstrate almost conclusively, however, even in the case of the photochemical change which exhibits the greatest departure from Einstein's law of photochemical equivalence, the validity of Draper's law.

[1] A general review of photochemistry, and its related fields, and a preliminary thermodynamic discussion followed by a historical review of the development of photochemistry and descriptions of such phenomena as incandescence, luminescence, radiation and the sources of visible and ultraviolet radiation, high temperature measurements, and chemiluminescence is given by Ranc and Wurmser, Industrie chimique, 1919, *6*, 200, 237, 264, 292, 361; 1920, *7*, 109; Chem. Abs. 1920, *14*, 2585. Forty reactions are mentioned that are accompanied by light, and several of the more important are covered in detail as well as the causes of chemiluminescence. The photochemical equivalent law from the point of view of the Bohr-Einstein conception of light absorption is discussed by Stern and Volmer, Zeitsch. wiss. Photochem. 1920, *19*, 275; J. Chem. Soc. 1920, 118, ii, 461.

[1a] Lon. Ed. Dub. Phil. Mag., 1843, *23*, 401.

[1b] J. Chem. Soc. 1921, *119*, 653.

[1c] J. Chem. Soc. 1924, *125*, 1521.

The rays which have photochemical action are those which are absorbed by the reacting substance; the wave-length of the rays influencing both the velocity and the direction of the reaction. The velocity also increases with the intensity of the light source, and catalyzers may greatly affect both the velocity and direction of the reaction.

In drawing attention to the similarity of numerous catalytic and photochemical reactions, Bancroft [2] suggests that in contact catalysis the formation of definite or indefinite chemical compounds with the solid catalyst is not in itself the essential thing, but is merely the step in the formation of the free radical which is the real reacting substance. Ultraviolet radiation is considered also to aid in the formation of free radicals. The problem on the photochemical side is to determine what radicals are formed and what ultraviolet rays produce them. If, as seems probable, each chemical bond corresponds to one or more absorption lines, which will lie in the ultraviolet or infra-red in the case of colorless compounds, it should be possible, theoretically, to break or open any desired bond in any given substance by the use of suitable monochromatic light of sufficient intensity under favorable conditions. In other words, there is a possibility of developing an absolutely new technic for organic chemistry.

Various reactions which proceed ordinarily with a catalyst have been studied in its absence by Bourgoin,[3] using instead, exposure to the radiation of a quartz mercury lamp. Acetylene was oxidized to acetaldehyde and acetic acid, benzol to phenol, toluol to benzoic acid, and sulfur dioxide to the trioxide. Methyl and ethyl alcohols were also oxidized.

A number of cases in which radiation (ultraviolet, *A*-ray, X-ray) brings about the same reaction as treatment with ozonized air are considered by Fernau.[4] Sucrose in neutral, acid, or alkaline solution is inverted when subjected to ultraviolet rays. Egg-albumin, when exposed to the radiation from radium, is coagulated and ceric hydroxide sols are similarly coagulated. These actions are also brought about when the substances concerned are treated with ozone or hydrogen peroxide. Reactions which can be induced photochemically and electrochemically have been compared by Smiths and Aten.[5] Ultraviolet rays transmitted through quartz and the discharge from an ozonizer were used to produce photochemical electrochemical equilibria, leading them to conclude that the action of light and of the electrical discharge is the same, namely, a displacement of the equilibrium in the endothermal direction.

Plotnikow [6] has expressed the opinion that every element or compound which has a free valence electron is photochemically unsaturated, that the photoactivity is a periodic function of their atomic numbers,

[2] Ind. Eng. Chem. 1924, *16*, 270; Chem. Abs. 1924, *18*, 1225.
[3] Can. Chem. & Met. 1923, *7*, 95; Chem. Abs. 1923, *17*, 2084; J. S. C. I. 1923, *42*, 574 A.
[4] Kolloid Z. 1923, *32*, 89; J. Chem. Soc. 1923, 124, ii 601.
[5] Z. Elektrochem. *16*, 264; Chem. Abs. 1910, 1842.
[6] Chem. Ztg. 1920, *44*, 825; see also Chem. Ztg. 1919, *43*, 321, 337; Z. Wiss. Photochem. 1919, *19*, 1.

and that every photochemically unsaturated compound is photoactive. Light tends to convert the unsaturated into the saturated, and in the process energy may be either absorbed or evolved. In general the longer light waves influence the reactions in which there is a loss of energy, and the short waves those in which there is a gain. A photochemically inactive system may be made active by the addition of such substances as uranium, iron, and chlorine which are rich in valence electrons and which act as catalyzers. These are classified as contact, transfer, chemical and optical catalysts depending upon the manner in which they enter into reaction. According to Nazarov [7] photochemical effects are now usually regarded, at least as far as their initial stages are concerned, as photoelectric effects, and since the latter are independent of the temperature, and since, further, the velocity of a photochemical reaction depends on the mass of the activated molecules, and this on the velocity of activation, it follows that the temperature-coefficients of photochemical processes should be less than those of reactions occurring in the dark. It appears probable that the temperature-coefficient of a photochemical reaction is of a magnitude characteristic of the structure of the photochemical component which absorbs the light. Thus in the absorption of light by the molecules containing, as photochemical components, iodine or bromide, the temperature-coefficients have the same value, 1.40.

Banerji and Dhar [8] have determined the temperature coefficients for a number of reactions, both in the light and in the dark. They find that for the reaction $CCl_3CO_2H \rightarrow CHCl_3 + CO_2$ the temperature coefficient is 4.28 in the dark and 3.6 in the light. The reaction is unimolecular. The inversion of cane sugar with 1.95 N acid has a temperature coefficient of 3.82 in the dark and 3.4 in the light. For $NaNO_2 + I_2 + H_2O \rightarrow NaNO_3 + 2\,HI$, a bimolecular reaction, the temperature coefficients are 2.5 and 1.4 in the dark and the light respectively. The bimolecular reaction: $FeSO_4 + I + H_2O \rightarrow Fe(OH)SO_4 + HI$ has temperature coefficients for the dark and light of 3.45 and 2.0 respectively. The oxidation of oxalic acid by hydriodic acid is unimolecular with respect to the concentration of the acid. The temperature coefficient in the dark is 2.98 and in the light it ranges from 2.2 to 2.5.

A consideration of results obtained by Berthelot and Gaudechon [9] shows that photochemical reactions can be divided into two classes, as is also the case with thermochemical reactions, namely (a) exothermic and irreversible, and (b) endothermic and reversible. In both cases the efficacy of the radiations used increases with their frequency, which consequently plays the part of potential or of "photochemical temperature." Endothermic changes which are produced thermally only by very high temperatures likewise are produced photochemically only by the extreme ultraviolet rays. Light tends to transform photochemically unsaturated compounds, i.e., those with unbound or weakly bound valence electrons, into photo-stable ones. Stereoisomers and intra-

[7] J. Russ. Phys. Chem. Soc. 1915, *47*, 943; J. Chem. Soc. 1915, *108*, ii 754.
[8] Z. Anorg. Algem. Chem. 1924, *134*, 172; Chem. Abs. 1924, *18*, 2634.
[9] Compt. rend. 1912, *154*, 1597; J. Chem. Soc. 1912, *102*, ii, 616.

molecular changes are the first stage in such a transformation. By systematic photolysis with suitable frequencies all members of the unsaturated organic classes (acids, aldehydes, alcohols, ketones, diazo compounds) can eventually be converted into hydrogen, carbon monoxide, carbon dioxide, nitrogen and saturated cyclic or open-chain compounds of the paraffin series. In case of more complex reactions photo-equilibria are set up which may be shifted in either direction by radiation of different frequencies. The stability of the hydrogen compounds with the members of the chlorine and oxygen groups of elements towards light of different wave-length led Berthelot and Gaudechon [10] to interesting conclusions. As in the case of decomposition by heat, it holds good that, in the same family of elements, the stability of the hydrogen compounds with respect to light decreases as the atomic weight increases. As previously noted, substances which are only dissociated at high temperatures are similarly only affected by the very rapid vibration of the extreme ultraviolet. Hydrogen chloride requires ultraviolet of wave-length 2000 Å for decomposition, while even then the change is slow. Under similar conditions hydrogen bromide is rapidly and completely decomposed. Hydrogen iodide is decomposed by blue and violet light. A similar relationship is found in the case of water vapor, hydrogen sulfide, selenide and telluride. This rule holds good in the case of the nitrogen and carbon groups.[11]

It is noted by Tian,[12] in experiments on the effect of ultraviolet radiation on water,[13] that the endothermic combinations produced by rays of short wave-length (1900 Å) are often destroyed by other ultraviolet radiations. In making ozone, or in other processes which use short waves, it is necessary to avoid those rays which tend to restrict the reaction. When quartz lamps are used they must be operated at a low voltage. Tian [14] finds the velocity of decomposition of hydrogen peroxide (in dilute aqueous solution) increases with the increasing frequency of the exciting radiation, and when thin layers of solutions of varying concentration are exposed to the rays emitted by a quartz mercury lamp, the velocity is proportional to the intensity of the incident radiation and not to the absorbed radiant energy. This result is attributed to the heterogeneity of the radiation and the fact that rays of different wave-length are not absorbed in a constant ratio. Whereas ultraviolet rays of moderately short wave-length are able to bring about the decomposition of hydrogen peroxide at a measurable rate, pure water is only decomposed by rays in the extreme ultraviolet.

[10] Compt. rend. 1913, *156*, 889.
[11] Compt. rend. 1913, *156*, 1243; J. Chem. Soc. 1913, *104, ii*, 458.
[12] Compt. rend. *156*, 1063.
[13] From experiments on the action of ultraviolet rays on water Kernbaum, Farm. Polsk. 1913, *16*, 71, concludes that water undergoes decomposition. Experiments indicate that the sun rays will act on water in the same way. Distilled water free from air, when exposed in a quartz vessel to the sun's rays, shows evolution of gas after a few hours. Using Shonbein's reagent, hydrogen peroxide may be detected. The quantity is larger when the experiments are carried out in presence of air, as is shown by the blue tint of the fluid in the quartz vessel.
[14] J. Chem. Soc. 1915, *108, ii*, 828; J. Chem. Ind. 1916, *35*, 114; Chem. Abs. 1916, *10*, 1960.

If the water contains dissolved oxygen, this reacts with the hydrogen set free in the primary photochemical decomposition of the water. At the same time, the dissolved oxygen is to some extent transformed into ozone under the influence of the ultraviolet rays, and the ozone formed reacts with the hydrogen peroxide. Experiments have shown that ozone has no action on water under these conditions. Investigations subsequently performed by Kornfeld [15] indicate that with increasing dilution the velocity is increasingly dependent on the concentration. The addition of acid also causes a diminution of the velocity which depends on the amount of acid added.[16]

Various investigators have observed the presence of hydrogen peroxide in solutions of radioactive salts, but, in considering the absorption of ultraviolet rays by radioactive elements and their degradation products, Zelinsky regarded the part played by the hydrogen peroxide formed under the influence of radium as small. Rosanoff [17] investigated the absorption spectra of ultraviolet by solutions of hydrogen peroxide and advances the suggestion that the absorption of short waves by radioactive substances is conditioned by the emanation developed, and by the hydrogen peroxide formed under the influence of this emanation. Henri and Wurmser [18] have made a study of the photochemical decomposition of hydrogen peroxide by monochromatic rays from the ultraviolet portion of the spectrum. The results show that the reaction is unimolecular, and that the velocity of decomposition is proportional to the concentration. For each wave-length the velocity is proportional to the incident energy. These investigators [19] further state that the addition of traces of numerous different substances to hydrogen peroxide renders it stable towards ultraviolet rays, alkalies being more active than acids in this respect, and suggest that in many of the cases of catalysis by ferments and colloidal metals, the action of poisons is on the substances undergoing transformation, and not on the catalyst itself. The action of certain ferments is quite comparable to that of the ultraviolet rays.

The effect of a number of organic compounds in inhibiting the decomposition of hydrogen peroxide by ultraviolet radiation is of interest to investigators in the field of ultraviolet. Anderson and Taylor [20] made determinations over regions of wave-length extending from the visible spectrum to lower limits corresponding to 200, 265, 293 and 305 μμ (2000, 2650, 2930 and 3050 Å). In most cases the inhibition is associated with the absorptive capacity of the compounds for the ultraviolet, and in the case of benzol, several esters, amides, ketones and alkaloids these factors are correlated. Amines and alcohols do not absorb strongly in the regions causing the decomposition of the peroxide, and it is

[15] Z. wiss. Photochem. 1921, *21*, 66.

[16] That Einstein's equivalent law does not hold was confirmed by Kornfeld. In the most favorable case one quantum brings about the decomposition of eighty molecules.

[17] J. Russ. Phys. Chem. Soc. 1912, *44*, 1146; J. Chem. Soc. 1912, *102*, *ii*, 875.

[18] Compt. rend. 1913, *157*, 126.

[19] Compt. rend. 1913, *157*, 284.

[20] J. Am. Chem. Soc. 1923, *45*, 650.

thought probable that esterification, with the hydrogen peroxide acting as a weak acid, may account for the inhibition. The following is a summary of the inhibition constants, the inhibitors being placed in the same solution as the peroxide:

Substance	Conc.	Regions of Wave-length to 2000	to 2650	to 2930	to 3050
Acetic acid	0.005	75	100	100	100
Phenylacetic acid	0.001	13	45	80	100
Hydrocinnamic acid	0.003 approx.	12	40	70	100
Benzoic acid	0.005	9	...	...	100
Ethyl acetate	0.005	100	100	100	100
Ethyl benzoate	0.001 approx.	14	50	80	100
Ethylphenyl acetate	0.001 approx.	17	70	85	100
Ethyl cinnamate	0.0002 approx.	25	45	65	100
Methyl oxalate	0.005	10	20	35	70
Methyl benzoate	0.005	9	...	...	...
Ethylamine	0.005 approx.	5	0	0	0
Aniline	0.005	7	0	0	0
Benzylamine	0.005	8	0	0	0
Acetamide	0.005	65	100	100	100
Benzamide	0.003	9	...	...	...
Acetanilide	0.0001	60	100	100	100
Ethyl alcohol	0.005	35	35	35	35
Phenol	0.002	0	0	0	0
Benzyl alcohol	0.0033 approx.	8	25	40	40
Acetone	0.005	70	60	55	50
Acetophenone	0.0002	11	40	65	100
Benzophenone	0.0001	45	60	100	100
Benzene	0.005	20	...	70	...
Quinine hydrochloride	0.0002	9	20	10	0
Quinine salicylate	0.0002	4	0	0	0

The value may be interpreted as follows: 80 to 100, extremely weak or no inhibition; 50 to 80, weak inhibition; 30 to 50, moderate inhibition; 20 to 30, fairly strong inhibition; 10 to 20, strong inhibition; 0 to 10, very strong inhibition.

The inhibitors act more efficiently when in the hydrogen peroxide solution than when employed as screening solutions. The explanation of this effect possibly lies in the ability of one quantum to decompose more than one molecule. Thus, if the stabilizer be acting as a screening solution, the peroxide being free from inhibitors, one quantum of radiant energy may slip through, enter the peroxide solution, and by successive activation decompose a number of molecules. On the other hand, if the stabilizer be in the peroxide solution, and one quantum of radiation should succeed in activating a peroxide molecule, this molecule will decompose, liberating again the quantum. This may activate another peroxide molecule or, coming within the sphere of influence of a molecule of inhibitor, may be converted into more harmless infra-red.

Other investigators likewise have studied the effect of various substances on the rate of decomposition of hydrogen peroxide in ultraviolet radiation. Mathews and Curtis [21] report that acetamide, carbamide, boric acid and barium chloride have no action on the rate of decomposition; acetic acid, tartaric acid, phosphoric acid, sulfuric acid, potassium

[21] J. Physical Chem. 1914, *18*, 521; J. Chem. Soc. 1914, *106, ii*, 602.

nitrate, potassium chloride and sodium chloride exercise a slight retarding action; benzoic acid, calcium hydroxide, sodium hydroxide and barium hydroxide exercise a strong retarding action, and barium nitrate increases the rate of decomposition. These results are not entirely in harmony with those of Anderson and Taylor,[22] whose conclusions are that inorganic bases are excellent inhibitors of the decomposition of hydrogen peroxide by ultraviolet rays, inorganic acids are good inhibitors, bromides and chlorides have a moderate inhibitory action, while other inorganic salts such as nitrates, sulfates, perchlorates, have no action. The inhibition is a function of the concentration of the hydrogen, hydroxyl, bromide and chloride ions respectively. Walton [23] and Schöne [24] found that chlorides were slowly decomposed by aqueous solutions of hydrogen peroxide with the formation of hypochlorites. Auger [25] and Sperber [26] report, however, that hydrogen peroxide reacts slightly with all the halogen acids and salts with the liberation of the free halogen itself. Anderson and Taylor believe that the action of continuously liberated chlorine and bromine from chlorides and bromides respectively may account in part for the inhibitory power of these ions, but a complete solution of the problem of inhibition appears to be much more complex.

Any theory to account for the inhibitive action by hydrogen, hydroxide, chloride and bromide ions must be in accord with the following facts. (1) The ratio of inhibitive efficiency of hydroxide to hydrogen ions is about 1 to 25; that is, 1 hydroxide ion inhibits as much as 25 hydrogen ions. (2) Hydroxide ions increase the concentration of peroxide ions in the solution by the formation of ionized peroxide salts. Hydrogen ions decrease the ionic dissociation of the hydrogen peroxide by common ion effect. (3) Inhibition has a zero temperature coefficient. (4) Inhibition is dependent on the concentration of hydrogen peroxide in solutions employed, 0.1 N to 6.0 N, and of wave length of incident radiation. (5) One $h\nu$ may decompose as many as 80 molecules of hydrogen peroxide. (6) Chloride ions are better inhibitors than bromide ions. (7) Alkali and alkaline earth cations, sulfate, perchlorate and nitrate ions and the undissociated molecules of acids, bases and salts do *not* inhibit.

Curtis [27] states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury lamp, neither are they bleached by the addition of 3 per cent hydrogen peroxide to them until the mixture is rayed.[28] To be sure that the bleaching was due to hydrogen peroxide and not to ozone, solutions of the dyes were submitted to radiation while a stream of oxygen was bubbled in but there was no bleaching in this case, hence it appears that the oxidizing power of hydrogen peroxide with respect to the bleaching of dyes is increased by exposing the mixture to rays of short wave-lengths. On the other hand, Holmes [29] reports that solutions of magenta, malachite green,

[22] J. Am. Chem. Soc. 1923, *45*, 1210.
[23] Z. Physik. Chem. 1904, *47*, 185.
[24] Ann. 1879, *195*, 228.
[25] Compt. rend. 1911, *152*, 712.
[26] Seweiz. Apoth. Ztg. 1914, *52*, 2, 245.
[27] J. Amer. Chem. Soc. 1920, *42*, 720; J. Chem. Soc. 1920, *118*, *ii*, 342.
[28] The rate of bleaching of the mixtures was followed by means of a Helige-Leitz colorimeter.
[29] J. Am. Chem. Soc. 1922, *44*, 1002.

methyl violet, and crystal violet, which have been decolorized by sulfur dioxide, when exposed to ultraviolet of wave-length between 220 μμ (2200 Å) and 330 μμ (3300 Å) develop their original colors. Comparison of the absorption spectra of the original dyes and those which had regained the color showed that the regained color is due to the original dye, since the absorption spectrum is the same in both cases. The reaction with sulfurous acid is reversible and consists of a decolorizing action and a colorizing action, the latter being photochemical. The large quanta of energy supplied by the ultraviolet rays cause the photochemical action to increase and consequently a displacement of the position of equilibrium occurs. The equilibrium position can also be displaced by chemical and thermal means.

The law of inverse stability of compounds in relation to their increase in molecular weight has been verified by experiments on the compounds of the nitrogen and carbon groups when under irradiation.[30] With a large 220-volt mercury lamp an almost complete decomposition of ammonia was obtained in two hours. With hydrogen phosphide decomposition was evident in a few minutes. Hydrogen arsenide, zinc ethyl and carbonyl chloride were readily decomposed, while sulfur fluoride and methane were scarcely attacked.

According to Stock and Friederici,[31] when boron hydride B_4H_{10} is preserved at room temperature over mercury, it slowly undergoes decomposition, with the formation of the hydride, B_2H_6. The decomposition is not appreciably affected by sunlight, but is accelerated to a great extent by ultraviolet rays. At 100° the decomposition is complete in a few hours, whereas at ordinary temperature it takes a month or more.

When rayed with ultraviolet, sulfur dioxide alone or mixed with oxygen, yields free sulfur and sulfuric acid.[32] (See Chapter 6.)

On exposure to ultraviolet radiation sulfuryl chloride breaks down into sulfur dioxide and chlorine; these substances absorbing rays of very different wave-lengths. This fact led LeBlanc, Andrich and Kangro [33] to investigate photochemical changes which take place in the system: $SO_2Cl_2 \rightleftarrows SO_2 + Cl_2$ under the influence of radiations of known wave-length. The absorption by chlorine reaches a maximum about 340 μμ (3400 Å) and is almost zero at 290 μμ (2900 Å). The maximum absorption by sulfur dioxide takes place at this point with a minimum at 240 μμ (2400 Å). For sulfur oxychloride absorption begins at 300 μμ (3000 Å) and rises rapidly for the shorter wave-lengths. An approach to equilibrium in the dark is possible only with catalyzers, and side reactions make the experiments not strictly quantitative, although these are probably much lower than 10 per cent of the total. When using radiations which are absorbed by sulfur oxychloride only, that component suffers practically complete decomposition both at 55° C. and 100° C. With mixtures of sulfur dioxide and chlorine the radiations absorbed by the former cause only slight changes

[30] Compt. rend. 1913, *156*, 1243.
[31] Ber. 1913, *46*, 1959.
[32] Compt. rend. 1910, *150*, 1517.
[33] Z. Elektrochem. 1919, *25*, 229; Chem. Abs. 1920, *14*, 493.

which are probably side reactions and not the formation of sulfur oxychloride, while radiations which are absorbed by chlorine only cause the reaction to run to an equilibrium, the position of which depends on the temperature and the moisture content.

Germann,[34] examining the inorganic reactions of phosgene, notes that the apparent activity of this reagent is much enhanced under conditions (temperature or ultraviolet radiation) which produce appreciable dissociation into chlorine and carbon monoxide, but this complication does not arise in experiments carried out below 200° in glass vessels.

Kuhn[35] states that when ultraviolet rays of wave-length 202.5 to 214.0 μμ (2025 to 2140 Å) fall on the compound $2AgCl \cdot 3NH_3$ the ammonia is decomposed. From 2 to 2.5 quanta are absorbed for each molecule decomposed and the rate of photochemical decomposition is independent of the temperature, extent of the quartz surface or the presence of sodium metal. When monochromatic light of wave-length 206.3 μμ (2063 Å) is employed the number of quanta increases to 3.4 or even to 10 with especially good separation of wave-lengths. This increase may be explained by the fact that the quantum $h\nu$ for wave-length 206.3 μμ (2063 Å) is 128,000 calories per gram mol, enough for the reaction

$$NH_3 \rightarrow N + H_2 + H - 123{,}000 \text{ cal.}$$

but insufficient for the reaction

$$NH_3 \rightarrow N + H + H + H - 207{,}000 \text{ cal.}$$

The rate of photochemical decomposition of ammonia (20-500°) is independent of the pressure, between 30 and 300 mm.[36] It rises with increase of temperature, but to a less extent than for most chemical changes. The rate falls off as decomposition proceeds, is decreased in presence of hydrogen, but is unaffected by the presence of nitrogen. This is due to the fact that molecular hydrogen, but not molecular nitrogen, is capable of reacting with activated ammonia molecules. Solutions of ammonia[37] in the presence of pure oxygen or of air when exposed at a temperature of 35° to 50° C., for from 3 to 9 hours at a distance of 3 to 6 centimeters from a lamp of 110 volts, are oxidized to nitrites. Nitrates are in no case formed. Ammonium salts are also oxidized to nitrites, the reaction being slower in the cases of the sulfate and chloride than in that of the carbonate. Air or mixtures of nitrogen and oxygen when exposed to ultraviolet rays are not appreciably affected. Nitrous oxide alone or mixed with oxygen produces nitric acid.[38]

In order to test the applicability of the Einstein photochemical law to photolysis in aqueous solution, Warburg[39] has examined the change

[34] J. Phys. Chem. 1924, *8*, 879.
[35] Compt. rend. 1923, *177*, 956; Chem. Abs. 1924, *18*, 789.
[36] Kuhn, Compt. rend. 1924, *178*, 708.
[37] Compt. rend. 1911, *152*, 522.
[38] Compt. rend. 1910, *150*, 1517.
[39] Sitzb. Preuss. Akad., Math.-Phys. Kl. 1918, 1228; Chem. Abs. 1920, *14*, 1930.

of nitrates to nitrites brought about by selected wave-lengths from the zinc spark and the mercury arc. The reaction proceeds most favorably in slightly alkaline solution, and except in highly concentrated solutions the degree of alkalinity does not affect the rate of reaction. The rate of reaction increases with the concentration of the nitrate, the reaction being greater for short than for long wave-lengths, oxygen in all cases being liberated.

According to Baudisch and Mayer [40] when aqueous solutions of potassium nitrate are exposed in a flat dish to the rays of a mercury lamp, oxygen is very soon liberated, a blue coloration from starch and potassium iodide being produced in five to ten seconds. The interposition of a glass plate delays change for twenty minutes. Aloin, which becomes red, may also be used.

Anderson [41] reports that aqueous solutions of potassium nitrate are decomposed by ultraviolet radiation of 333 μμ (3330 Å) and shorter wave-length. The reaction is accelerated by heat, and the products of decomposition are potassium nitrite and oxygen, but the reaction is auto-inhibited by the nitrite and "a steady state" is reached when only a small quantity of nitrate has been decomposed, while the addition of nitrite to a solution of potassium nitrate partly or completely inhibits the photolysis of the latter. Aqueous potassium nitrite solutions are stable in ultraviolet radiation. Potassium nitrate solutions obey Beer's Law; consequently nitrate-nitrite equilibria are different in stirred and unstirred solutions, the difference depending on the concentrations. In unstirred solutions, the equilibrium depends entirely on the size of the surface exposed to the radiation, and on the concentration and thickness of the solution. Alkali hydroxides increase the rate of photolysis and displace the "steady state" towards the nitrite, possibly owing to the formation of a peroxide. Acids decrease the rate of decomposition, but do not displace the "steady state."

Dutoit [42] and Nicollier [43] have found that although the conductance of acetophenone does not change under the influence of light, the conductance of solutions of sodium iodide and lithium bromide in this solvent decreases, when exposed to light, to a constant value, and then increases when these previously exposed solutions are placed in the dark. Furthermore, a yellow color which develops in the light disappears in the dark. These investigators conclude that the reactions are reversible. On repeating these experiments in glass, using sunlight, Morgan, Lammert and Crist [44] confirm the results of Dutoit and Nicollier, but find that solutions which have reached a constant conductance value in glass, continue to react, the conductance again decreasing, when placed in quartz vessels and exposed to light. Furthermore, using a mercury vapor lamp and glass apparatus, they find that acetophenone is decomposed with the formation of benzoic acid,

[40] Ber. 1912, *45*, 1771.
[41] J. Amer. Chem. Soc. 1924, *46*, 797.
[42] Z. Elektrochem. 1906, *12*, 640.
[43] Thesis, with Dutoit and Lausanne, 1907.
[44] J. Am. Chem. Soc. 1924, *46*, 1170.

and that when salts such as sodium iodide are present, iodine is liberated in a quantity independent of the concentration of sodium iodide, and dependent upon the intensity of the radiation and time of exposure, that is upon the quantity of acetophenone decomposed.

In an investigation of the stability of potassium iodide, nitrate and chlorate, Suryanarayana [45] found that an aqueous potassium iodide solution, with starch indicator, and with the addition of various acids turns blue on exposure to either diffused or direct sunlight. The time interval varies according to the acid employed, being shortest with hydrochloric and increasing in the order, sulfuric, oxalic, tartaric and acetic. When air or oxygen is excluded the reaction does not take place, even when exposed to ultraviolet rays. Neutral potassium chlorate and potassium nitrate solutions on exposure to ultraviolet liberate oxygen, but equilibrium is quickly established. An excess of potassium nitrite prevents the decomposition of the nitrate. Exposure of a mixture of potassium nitrate or chlorate and iodide to ultraviolet with the exclusion of oxygen results in the decomposition of the nitrate or chlorate and consequent oxidation of the iodide.

It has been observed by Ross [46] that when a solution of potassium iodide is exposed in an open vessel to the ultraviolet radiation from a spark, the amounts of iodine set free for equal intervals of time varied greatly. When the distance of the solution from the spark was doubled, the rate of decomposition remained almost the same as before. The spark was then made to pass through an atmosphere of oxygen. This was done by placing the terminals in a large bell jar filled with the gas. Under these conditions, the rate of decomposition was found to be very much increased. In replacing the oxygen with carbon dioxide, the amount of decomposition resulting in the same length of time was very small. It therefore became evident that the greater part of the decomposition first obtained was produced, not by raying only, but principally by the action of ozone and the oxides of nitrogen formed by the passage of the spark through air. To determine the effect of the ultraviolet only, the solution was placed in a small shallow dish sealed with a quartz cover. When the dish was exposed the decomposition resulting represented the total effect of the radiant energy. By subtracting from this the effect produced when a thick piece of glass plate was interposed between the spark and the solution, the effect of the ultraviolet alone, or that part of it capable of being absorbed by the glass, was determined. It was found that the amount of iodine set free varied inversely as the square of the distance. Strontium iodide in neutral aqueous solutions decomposes, according to Kailan,[47] the most

[45] J. Sci. Assoc. Maharajah's College, Vizianagaram, 1924, *2*, 12; Chem. Abs. 1924, *18*, 3548.

[46] J. Am. Chem. Soc. 1906, *28*, 788.

[47] Chem. Abs. 1914, 14. The reaction $2Fe^{\cdot\cdot} + I_2 \rightleftarrows 2Fe^{\cdot\cdot\cdot} + 2I'$ is photosensitive to both ultraviolet and visible light, the latter within the range 5500—6500 Å., with an apparent maximum at 5800 Å. The tri-iodide ion is the photosensitive constituent and the energy of excitation is equivalent to 2.14 volts, almost identical with the resonance potential of the iodine molecule. One quantum of absorbed radiant energy causes 1 mol. of iodine to react. The dark

rapidly, while barium iodide seems to decompose faster than potassium and magnesium iodide, but when exposed to ultraviolet rays barium iodide and strontium iodide decompose faster than potassium iodide.

The action of rays of short wave-length on solutions of potassium iodate has been determined by Mathews and Curtis.[48] Solutions of potassium iodate were placed in a quartz flask and kept at a temperature of 30°; iodine was liberated. The following results were obtained: When the photolysis is carried out in the presence of air, the rate of the reaction slowly decreases with time. Iodine is not liberated when the solution is kept saturated with oxygen in an atmosphere of oxygen. Carbon dioxide greatly increases the rate of photolysis. Potassium iodate, in a solution kept saturated with carbon dioxide, gives a rate of photolysis which is linear when the amount of iodine liberated is small compared with the total amount present in the iodate.

The influence of ultraviolet rays on alkaline salts of acids containing halogen and oxygen has been compared by Oertel.[49] Under the action of ultraviolet the alkali salts of chlorates, bromates, iodates and periodates in aqueous solution decompose into oxygen and the halogenide, and the reaction is quantitative with a sufficiently long period of irradiation. Only a very small decomposition could be observed in the case of the perchlorates.[50] The rate of decomposition of bromates was greater than that of iodates. The latter decomposed at a rate greater than that of chlorates. The amount of reaction products formed in a given time increased with increasing concentration of the solution, and the nature of the cation was without influence on the rate of decomposition.

Marmier [51] has decomposed solutions of sodium thiosulfate, sulfur and hydrosulfite being formed. The latter in itself was rapidly decomposed by ultraviolet and after an exposure of 75 minutes under the conditions of the observation no traces remained.

Wolff [52] has examined certain specimens of calcined (dehydrated) potassium carbonate by means of ultraviolet radiation and these showed in places a livid red luminescence. The effect was traced to the presence of potassium sulfide. Exposure to ultraviolet rays affords a simple

equilibrium constant, $(Fe^{\cdot\cdot})\ (I_2)^{\frac{1}{2}}/(Fe^{\cdot\cdot\cdot})\ (I')$ is 23.6 at 25°. The ratio of the velocity constant of the liberation of iodine at 35° to that at 25° is 2.713, while for the photochemical reaction this ratio is 1.17. The addition of potassium chloride increases the thermodynamic concentrations of all the reactants, increasing the velocity of reaction thereby, but not affecting the final equilibrium. Rideal and Williams, J. Chem. Soc., 1925, *127*, 258.

[48] J. Physical Chem. 1914, *18*, 641; J. Chem. Soc. 1914, *106, ii*, 830.

[49] Biochem. Zeitsch. 1914, *60*, 480; J. Chem. Soc. 1914, *106, ii*, 321.

[50] A process for the electrolytic formation of perchlorates is described by Mack, J. Phys. Chem. 1917, 238, in which he states that chlorate may be oxidized to perchlorate in an acid solution by the use of sulfuric acid, ozone and hydrogen peroxide. But when hydrogen peroxide is used hydrochloric acid is produced and interferes with the oxidation. The reaction may be carried out with oxygen if activated by ultraviolet rays.

[51] Compt. rend. 1912, *154*, 32.

[52] Chem. Zeit. 1912, *36*, 197.

means of detecting even traces of this substance in commercial potassium carbonate. The salt must be dehydrated and cooled before examination. Mathews and Dewey [53] have studied the action of ultraviolet on solutions of sodium sulfite, potassium permanganate, potassium bichromate and oxalic acid. It was found that sodium sulfite solutions are not oxidized by the action of ultraviolet radiation in absence of air, but that the oxidation in presence of air is greatly accelerated by such rays. Potassium permanganate and potassium bichromate are very stable towards ultraviolet.

From a study of the photochemical properties of the chromates, Plotnikow [53a] concludes that neither ammonium, potassium nor sodium chromate suffers any transformation if exposed to the most intensive sunlight in the absence of substances capable of oxidation. In the presence of such substances, both of the organic and the inorganic type, the photochemical reduction of the chromates and dichromates takes place rapidly even in the arc light. The reduction results in either a brownish precipitate or a green solution according to the properties of the substance which serves as an oxygen absorber. In some cases there is an evolution of gas, either ammonia, in the case of ammonium chromates, or carbon dioxide.[54]

Rideal and Norrish [55] have studied the photochemistry of potassium permanganate. They find that potassium permanganate solution, on irradiation by ultraviolet, undergoes a marked change of electrode potential, which recovers slowly to its original value when the rays are extinguished. The change in the electrode potential is ascribed to an alteration in the p_H of the solution, brought about by a photochemical decomposition of the potassium permanganate. This decomposition makes itself apparent by the separation of a brown precipitate of the formula $K_2O \cdot 2\,MnO_2$, and the formation of a red sol of manganese dioxide and potassium manganite, in the solution. The electrode potential changes can be explained as a result of a production of potassium hydroxide in the solution by the photo-decomposition of the potassium permanganate, and a removal of the latter by combination with the hydrated manganese dioxide; as a result, a photochemical stationary state ensues. The decomposition is mono-molecular over the range of concentrations investigated. The addition of sulfuric acid to the permanganate solutions was found to hasten decomposition, and to impose a zero molecular law of decomposition on the solution. This change in the type of decomposition is connected with the non-formation of colloid in the acid solution. In continuation of this work Rideal and Norrish [56] have investigated the absorption spectrum of a 0.01 N-solution of potassium permanganate, more especially in the ultraviolet, in order to determine the wave-length of the light effecting the decomposition of potassium permanganate, and to test the validity of Einstein's

[53] Eighth Int. Cong. Appl. Chem., 1912, Sect. IX, Orig. Comm. *20*, 247.
[53a] Bull. acad. sci. Russ. 1919, 1093; Chem. Abs. 1923, *17*, 2231.
[54] A uviol lamp was used in the experiments.
[55] Proc. Royal Soc. A 1923, *103*, 342.
[56] Proc. Roy. Soc. A 1923, *103*, 366.

photochemical law in this connection. In the absorption spectrum, a band occurred between 380 and 270 μμ (3800 and 2700 Å) with its head at 313 μμ (3130 Å) while beyond 260 μμ (2600 Å) a second band commenced. The visible radiations of the mercury vapor spectrum were not appreciably effective in decomposing potassium permanganate, and it is considered that the line at 312.8 μμ (3128 Å) is principally responsible for the photo-decomposition by mercury vapor radiation. Assuming that the only photo-active line is at 312.8 μμ and that the coefficient of absorption for green and yellow light is the same as for the ultraviolet, two quanta are probably concerned in the photo-decomposition of the permanganate ion. It was found that mixtures of potassium permanganate and oxalic acid were much more sensitive to ultraviolet rays than to visible light.

Calcium carbide was exposed to the action of ultraviolet rays by Custis.[57] There was apparently no reaction as no pressure was built up and the tests for ammonia in the treated product gave negative results. Solutions of bleaching powder lose their available chlorine with great rapidity on exposure to tropical sunlight.[58] The effect is much more marked in the case of dilute solutions than it is in strong solutions.

The action of ultraviolet rays on ferric sulfate, nitrate and chloride is noted by Ross,[59] who used an arc between aluminum electrodes as a source of ultraviolet. The action on ferric salts is much increased by the presence of some organic compound, as cane sugar, which of itself will not reduce these salts but does so under the influence of radiation. The amount of ferric salt reduced is approximately proportional to the time of exposure.

Varying the temperature of any ferric salt solution was found to have a slight effect on the rate of reduction. It has been shown that (methyl) alcoholic ferric chloride is reduced in sunlight; ferrous chloride, hydrogen chloride, and formaldehyde being the primary products while methyl chloride and formaldehyde compounds are obtained by secondary reactions. If the radiation acts merely catalytically, the velocity of the reaction should be proportional to the concentration.

Benrath[60] and others define a purely photochemical reaction to be one which does not proceed in the dark and when exposed to light the rate is proportional to the amount of light energy absorbed. It follows that with constant illumination the rate of the reaction is proportional to the time of exposure. The reduction of ferric chloride by alcohols is a simple photochemical reaction. This is also the case when the reduction is affected by tartaric, citric and oxalic acids and by glycerol. Using a mercury vapor lamp as the source of radiation, the rate of reduction of such solutions of ferric chloride in quartz vessels is about double that in glass vessels.[61]

[57] J. Frank. Inst. 1917, *184*, 880.
[58] Fowler, J. Chem. Soc. 1908, *94*, *ii*, 914.
[59] J. Am. Chem. Soc. 1906, *28*, 790.
[60] Zeitsch. physikal. Chem. 1910, *74*, 115; J. Chem. Soc. 1910, *98*, *ii*, 813.
[61] A catalytic radiation reaction, at least of this type, therefore may be defined as one which proceeds slowly without exposure and is accelerated by raying.

Under the influence of light, copper combines with chlorine [62] but not with bromine or iodine; with oxygen, but not with sulfur; with water, but not with hydrogen sulfide; with ammonia, but not with phosphine or arsine. Aqueous solutions of the chlorides or sulfates of gold, silver, uranium, copper, nickel, chromium and cobalt are reported by Berthelot and Gaudechon [63] to be unaffected by ultraviolet irradiation. The sulfates of nickel and cobalt give a slight brown precipitate but this is due to the presence of traces of iron. Solutions of ferrous sulfate give a precipitate of the basic salt. Ferric sulfate does not give a precipitate when pure but in the presence of nickel or cobalt sulfate gives a precipitate of the basic salt. Urbain and Scal [64] state that rays from an arc, in passing through tetrachloride of titanium, of tin, or of carbon, cause a marked decomposition, chlorine being liberated.

According to Byk, Fehling's solution is decomposed by light of wave-lengths less than 400 μμ (4000 Å) corresponding with an absorption band in the ultraviolet, whereas the red and yellow waves of the visible absorption bands have no action. This is contrary to the rule that radiations which are absorbed by a substance tend to destroy it. It is suggested that the red light absorbed by Fehling's solution is not active enough, unaided, to produce decomposition, whereas in presence of a suitable reducing agent its activity might be sufficiently reinforced for it to do so. In accordance with this suggestion Leighton [65] finds that in presence of quinol within certain very narrow limits of concentration Fehling's solution is reduced by red light, but is stable in the dark.

Various inorganic and organic substances have been investigated by Michaud [66] with the object of noting their behavior toward ultraviolet. Zinc oxide, bismuth subnitrate and cerium carbonate were found not to reflect the rays while dark inorganic compounds exhibited reflecting properties.

When an alcoholic solution of hydrogen sulfide is gradually added to mercury halides in suspension or solution, according to Varalalu, Ram and Rao,[67] complex compounds of the general formula $HgX_2 \cdot 2HgS$ result. These compounds, showing various shades of red and yellow, undergo a color change readily in direct or diffuse daylight, regaining their original colors in the dark. Halogen mercury thiocyanates are likewise phototropic, and complex halides of mercury such as HgIBr, HgICl, and HgBrCl are somewhat less so. Cinnabar appears to be decomposed by the ultraviolet rays of direct sunlight, into its elements.[68] On exposure, the surface color rapidly turns to bluish gray, and this change proceeds slowly throughout the mass.

Pougnet [69] exposed a solution of mercuric chloride in a quartz tube to a mercury vapor lamp and almost immediately it became cloudy,

[62] Compt. rend. *157*, 129.
[63] Compt. rend. *152*, 376.
[64] Compt. rend. 1919, *168*, 887.
[65] J. Physikal. Chem. 1913, *17*, 205; J. Chem. Soc. 1913, *104, ii*, 459.
[66] Arch. Sci. Phys. Nat. 1912, *33*, 498.
[67] J. Sci. Assoc. Maharajah's College, Vizianagaram 1924, *1*, 107; Chem. Abs. 1924, *18*, 3529.
[68] Cropp, Proc. Austral. Inst. Met. 1923, No. 52, 259.
[69] Compt. rend. 1915, *161*, 348; J. Soc. Chem. Ind. 1915, *34*, 1053.

owing to formation of calomel. After 30 minutes, 42 per cent of the mercuric chloride had been decomposed and the calomel began to darken. After 70 minutes, when 48 per cent of mercuric chloride had been decomposed, the reaction ceased. The reaction is reversible. Skinner [70] finds that mercurous sulfate darkens rapidly on exposure to light and this result is due chiefly to the short light rays, and is independent of the presence of air. The rays from radium bromide have a similar effect, the mercurous salt phosphorescing very slightly under the action of the rays. Skinner does not favor the view that the darkening is due to the production of mercury and mercuric salt, and it is suggested that a dark sub-salt may be formed or that a polymeric modification may be produced.

The rate of reduction of mercuric chloride by ferrous chloride under different conditions has been examined in some detail by Winther.[71] When the concentration of the mercuric chloride is constant and relatively small, the rate is nearly independent of the concentration of the ferrous salt. For a given concentration of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum appears to be attained when the two salts are present in equimolar quantities. In the case of solutions containing small quantities of mercuric chloride relatively to ferrous chloride, the sensitiveness increases with the dilution, but this is not the case for solutions containing equimolar quantities. Such solutions do not vary to the same extent when the concentration is changed, and the maximum sensitiveness is shown by a solution containing the two salts in 3-molar concentration. The presence or absence of oxygen is without appreciable influence on the equimolar solution, but oxygen reduces the quantity of mercurous chloride obtained when a large excess of ferrous chloride is present. The most active rays are those of wave-length less than 265 μμ (2650 Å) as is shown by comparative experiments in quartz, uviol glass, and ordinary glass vessels.

Boll [72] has studied the rate of hydrolysis of tetrachloroplatinic acid when submitted to rays of different energy, the amount of radiation reaching the acid solution being controlled by a cell containing a dilute solution of caffeine, the concentration and thickness of the layer being varied. A later study by Boll [73] of the photochemical decomposition of chloroplatinic acids in very dilute aqueous solution, shows the progress of the photochemical reaction by measuring the increase in the electrical conductivity of the solution.

Ritter [74] showed that chloride of silver was blackened by ultraviolet rays, and that the effect was reversed by the invisible rays beyond the red. Hörig [75] observed that a strip of silver foil, heated by an electric current and exposed during the heating and subsequent cooling to ultraviolet radiation cools more rapidly than a foil similarly heated and cooled in the dark.[76] No such effect could be found with a platinum-iridium foil.

[70] Proc. Camb. Phil. Soc. 1904, *12*, 260; J. Chem. Soc. 1904, *86, ii*, 173.
[71] Zeitsch. wiss. Photochem. 1912, *11*, 60.
[72] Compt. rend. 1914, *156*, 138; J. Chem. Soc. 1913, *104, ii*, 171.
[73] Ann. Physique 1914 (ix), *2*, 54, 266; J. Chem. Soc. 1915, *108, ii*, 123.
[74] Nicholson's Journal *8*, 214, 1804.
[75] Physik. Z. 1916, *17*, 178.
[76] Temperatures were measured by a thermocouple.

The surface of a metal, whether from oxidation or from some other cause, changes with lapse of time so as to make the metal more electronegative. For example, Anderson and Morrison [77] found the contact difference relative to a plate of uncleaned copper was 0.060 volt for freshly-cleaned copper, 0.466 volt for uncleaned zinc, and 0.826 volt for freshly-cleaned zinc. It has been found that when exposed to a powerful source of ultraviolet rays, zinc becomes decidedly more electronegative, the effect disappearing slowly when the source of radiation is removed. Allen [78] states that iron which is chemically active shows a relatively large photoelectric activity, as it loses a negative charge fairly rapidly when insulated and irradiated by ultraviolet. Processes which render the iron passive greatly reduce this activity.[79]

Gortner [80] exposed several specimens of glass from various sources to the direct action of the sun, and made following observations: Glass which is relatively rich in manganese (about 0.2-0.3 per cent) becomes colored in less than a month, the degree of coloration being proportional to the manganese present. Most specimens of glass containing only a small proportion of manganese become colored in less than a year and the color becomes deeper if the time of exposure is increased. The production of this violet coloration is a proof of the presence of manganese, but some specimens of glass, although containing this element, do not become colored. A violet background is more favorable to the action of ultraviolet rays than any other color. White, yellow, red, and blue act alike, and seem to have no effect on the rate of coloration, while brown and black appear to have a retarding action. Fischer [81] has exposed various kinds of glass to ultraviolet rays from a quartz mercury lamp, the short space between the quartz and glass being filled with hydrogen. Jena combustion glass, Durax glass (Schott), German lead glass, and English lead glass were not affected, whereas ordinary Thuringian glass, apparatus glass from Greiner, apparatus glass from Bock and Fischer, and normal thermometer glass (Schott) were colored strongly violet within 12 hours. All the latter contained manganese, whereas the glasses which were not discolored were free from manganese. The violet color is readily destroyed by heating the glass until it softens.

A record of a large number of observations relating to the changes in color of various minerals and colored glasses on exposure to the action of radium rays and ultraviolet radiation is given by Doelter.[82] It follows from the results obtained that, generally speaking, the coloring materials of minerals are not of an organic nature, the colors being due principally to the presence of oxides of iron, chromium and manganese. The change in color under the influence of radium rays is in many cases the outcome of a reducing action while the ultraviolet

[77] Phil. Mag. 1912, *24*, 302.
[78] Faraday Soc., Nov. 12, 1913.
[79] These facts are in good agreement with the theory that the cause of passivity is to be found in the presence of a gaseous layer on the metallic surface.
[80] Amer. Chem. J. 1908, *39*, 157.
[81] Ber. 1905, *38*, 946.
[82] Monatsh. 1909, *30*, 179; J. Chem. Soc. 1900, *96, ii*, 363.

rays have an oxidizing action; consequently ultraviolet and radium rays frequently induce opposite changes. This may have some bearing on the origin of the color of many minerals and precious stones.

The ultraviolet transparency of certain colored media is of interest from the standpoint of absorption. Absalom [83] makes the observation that many gems and minerals which in ultraviolet rays are transparent when colorless, do not lose their transparency in the colored specimens; nor is any effect noted on artificially coloring a specimen by means of cathode rays, although colored metallic salts and aniline dyes are opaque. This is strong evidence that the color of minerals is due to colloidal metals, especially in such cases as hyacinth (zircon) and yellow topaz. Deeply colored solutions of the alkali metals and magnesium in liquid ammonia also are extremely transparent in the ultraviolet, which tends to show that these metallic solutions are colloidal.

It has been shown by Murphy and Mathews [84] that the electrical conductivity of arsenic trisulfide hydrosol increases upon exposure to light, the rate of change increasing somewhat with decreasing concentration of the colloid. This is explained as being due to the increased photochemical activity of the colloid per unit mass of arsenic trisulfide, brought about by the greater dispersity of the more dilute solution. Colloidal solutions of arsenic have been prepared by Dede and Walther [85] by exposing arsenic hydride in distilled water to the action of a powerful source of ultraviolet radiation.

Röntgen, ultraviolet and α-radiations cause the coagulation of sols of cerium hydroxide and albumin, and the inversion of cane sugar solutions, according to Fernau.[86]

Wassiljewa [87] notes that if dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained, which in the presence of various organic substances, such as formaldehyde, sucrose, dextrose or dextrin, undergoes reduction on exposure to light, with the formation of an intense blue solution. If the undialyzed solution is kept for some time, it is found that the above reduction process does not occur when the solution is exposed to light. On raising the temperature, however, the blue reduction products are obtained, as in the case of the freshly prepared colloidal solution. It is suggested that this is due to the existence of two forms of colloidal tungstic acid, one of which is photochemically sensitive and the other inactive. The former changes spontaneously into the latter, but the reverse transformation is brought about by a rise of temperature. The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification.

Schulze [88] reports that experiments on the conversion of metals into

[83] Chem. Abs. 1917, *11*, 2556; Phil. Mag. 1917, 450.
[84] J. Am. Chem. Soc. 1923, *45*, 16.
[85] Ber. 1925, *58*, 99.
[86] Kolloid-Z. 1923, *33*, 89; Chem. Abs. 1923, *17*, 3837.
[87] Zeitsch. wiss. Photochem. 1913, *12*, 1; J. Chem. Soc. 1913, *104*, *ii*, 265.
[88] Ber. Physik. Ges. 1912, 246.

dust by means of ultraviolet radiation gave negative results.[89] Spear, Jones, Neave and Shlager [90] find that the coagulation of Bredig's platinum hydrosol is greatly hastened by exposure to a 220-v. Cooper-Hewitt quartz lamp at 15 cm. distance. A platinum solution which was not completely coagulated in 2 years in ordinary light was half coagulated in 10 hours in ultraviolet. The ultraviolet rays greatly accelerate the coagulation of the solutions by common salt and is more marked in dilute solutions. According to Slatineanu [91] the precipitation of gold and palladium may be effected by means of hydrogen previously irradiated with ultraviolet, for instance by passing the gas through a helical silica tube surrounding a silica mercury vapor lamp.

A curious method of depositing metals is that of Jacquier,[92] who describes a process of precipitating metals from solutions of their salts by treatment with ultraviolet rays in the presence of aluminum. The process may be assisted by sunlight. Mercury vapor lamps are suspended between aluminum plates in the tank containing the solution to be treated. Svedberg [93] has succeeded in preparing colloidal solutions of metals by the application of the observation of Lenard and Wolf [94] that certain substances, especially metals, are disintegrated when exposed to ultraviolet rays. Pieces of metal, the surfaces of which had been carefully freed from oxide, were placed in a shallow dish containing a dispersion oxide medium, and exposed to the rays from a Heræus quartz mercury arc lamp at a distance of a few centimeters. After a few minutes colloidal solutions were obtained from silver, copper, tin and lead, but platinum, aluminum and cadmium remained practically unaffected. The action was especially marked in the case of lead, which yielded a colloidal solution in ethyl alcohol, and a milky liquid, probably containing colloidal lead hydroxide, in water. Experiments with silver and lead in water, ethyl alcohol, isobutyl alcohol, ether, acetone, ethyl acetate, and amyl acetate showed that the nature of the dispersion medium had a great influence on the results. Following Svedberg's observation, Kimura [95] tested the effect of ultraviolet on silver, copper and an alloy of cadmium 90, antimony 10 per cent. In a vacuum no corrosion takes place, in air there is a very slight corrosion, in oxygen somewhat more, and in water strong corrosion, under the influence of the rays. Nordenson [96] continued these experiments of Svedberg and Kimura. A plate of silver was immersed in alcohol and exposed to ultraviolet radiation and the loss in weight determined from time to time. A qualitative investigation of the formation of colloids of metals when immersed in water, alcohol and other solvents and exposed to ultraviolet, Röntgen or radium rays showed that the action of Röntgen and radium rays was similar to, but weaker than that of ultraviolet

[89] Compare results obtained by Svedberg.
[90] J. Am. Chem. Soc. 1921, *43*, 1385.
[91] British Patent 157,785, Jan. 10, 1921.
[92] British Patent 17,790, Aug. 2, 1913.
[93] Ber. 1909, *42*, 4375; Zeitsch. Chem. Ind. Molloide, 1910, *6*, 129 and 238.
[94] Ann. Phys. Chim. 1889, *37*, 443.
[95] Kyoto, 1913, *5*, 253.
[96] Kolloidchem. Beihefte 1915, *7*, 110.

radiation. The colloid formation is ascribed to the activity of the rays in forming hydrogen peroxide which attacks the metal, yielding an oxide or hydrate, which in turn is dissolved in the crystalloid form, and is then converted to a metallic colloid by the reducing action of the rays.[97]

From the foregoing it will be evident that there is some difference of opinion in regard to the effect of ultraviolet rays on colloids.[98]

The properties of colloidal silver have been examined by Long,[99] the substance being obtained by the high frequency arc method. From a series of experiments in which the colloidal solutions were absorbed by filter paper and exposed to the action of ultraviolet radiation, it has been found that the more highly dispersed solutions are particularly sensitive to the action of the rays.

Light of short wave-length is reported by Davies [100] to catalyze the production of colored bands of colloidal gold in silicic acid gels containing gold chloride and various reducing agents.

In view of the effect of colored light upon plant growth and pigmentation, Gardner [101] suggested a study of the precipitation of lithopone under colored light or ultraviolet radiation. Believing that the coloration of zinc oxide in lithopone might be due to the presence of zinc sulfide, Nishizawa [102] mixed zinc sulfide and glycerol on paper and exposed it to the action of ultraviolet rays. There was no coloration of the zinc compound and it was found by similar experiments that other polyatomic alcohols have the same protecting properties. Certain organic salts such as zinc tartrate and Rochelle salts have a like effect, while some others are without influence. Magnesium and calcium hydrate also serve as protectors to the zinc compounds. It was shown that linseed oil and turpentine have no effect on this protective action, and that only minute quantities are necessary to afford complete protection. Based on the above experiments a new method of manufacture of lithopone was devised,[103] in which the zinc sulfide is treated with glycerol, or the saccharides, and salts and esters of tartaric and polyhydroxystearic acids. The sulfide may be incorporated with the organic compound itself, or with its aqueous solution. The sulfide may be precipitated in the presence of the organic compound, or the organic compound may be formed in the presence of the zinc sulfide. Prepared in this manner the sulfide shows no appreciable change when exposed for several hours to the action of ultraviolet rays or by gradually heating to a temperature of 120° C.

Roches [104] believes that the blackening of lithopone under the action

[97] It has been stated by Wiemarn that exposure to ultraviolet rays causes the size of the particles of colloids to be diminished.

[98] Zeit. angew. Chem. 1914, 18.

[99] Kolloid Zeitsch. 1914, *14,* 136; J. Chem. Soc. 1914, *106, ii,* 363.

[100] J. Am. Chem. Soc. 1923, *45,* 2261.

[101] Paint Manufacturers Assoc. of U. S., Circ. 98, June, 1920; Chem. Abs. 1920, *14,* 3698.

[102] J. Tokyo Chem. Soc. 1920, *41,* 1054; Chem. Abs. 1921, *15,* 1407.

[103] British Patent 156,971, Nov. 25, 1919. For a discussion of the behavior in ultraviolet light of various lithopones admixed with water, glycerol, oils and varnishes see Gardner and Holdt, Paint Manufacturers Assoc. Circ. 194, 1923.

[104] Rev. Chim. Ind. 1922, *31,* 109; Chem. Abs. 1922, *16,* 3217.

of sunlight (or ultraviolet rays) is due to the presence of impurities, and especially of chlorine, the addition of 0.002 per cent chlorine causing blackening in ultraviolet. The presence of iron, cadmium, cobalt, manganese and even radium does not cause blackening. The simplest and surest method of preventing the action of light, according to Roches, is to surround each particle of the pigment with a film of a substance on which light has no action such as zinc oxide, alumina, or barium sulfate.[105]

Maas and Kempf,[106] however, assert that the blackening of lithopone on exposure to light is due to the calcined zinc sulfide it contains. They conclude that the phenomenon is brought about by the change of zinc sulfide forming zinc disulfide and finely divided metallic zinc on the surface of the mass. The mechanism of the process, they consider, is the same as that referred to by Fajans in discussing the action of light on silver bromide.[107] The ultraviolet rays in the light cause the transference of an electron from a negatively charged sulfur-ion on the surface of the crystal lattice of zinc sulfide to a neighboring positively charged zinc-ion, whereby free uncharged atoms of zinc and sulfur are formed. The zinc appears as finely divided metal, the sulfur atom combines with neighboring zinc- and sulfur-ions to form zinc disulfide. Amorphous freshly precipitated zinc sulfide not possessing a lattice structure is not sensitive to light. Neither is zinc sulfide which has been ground in a mortar, since here the lattice arrangement has been disturbed. Blackened lithopone brightens in the dark owing to oxidation of the metallic zinc, for it remains black if no oxygen is present.

After a study of the darkening of certain zinc pigments Job and Emschwiller[108] conclude that all varieties of white zinc sulfide which blacken under the influence of light must have been heated; must contain at least traces of impurities, either metals or metalloids; and must not be entirely anhydrous. That the slate color of the exposed sulfide is rightly attributed to the presence of zinc has been established experimentally by allowing the radiation from a mercury arc to act on zinc sulfide suspended in water in a quartz vessel, whereby several cg. of zinc as well as sulfur were formed. Hydrogen was also liberated in the process due in part to the action of the zinc on water and in part to the formation of hydrogen sulfide which was decomposed by radiation. Some zinc salt of a thionic acid was also formed in the process. The sulfides affected were all phosphorescent and the rapidity of darkening was found to vary as the product of two factors: the intensity of the phosphorescence and the hygroscopicity. The sulfide with certain impurities is rendered metastable by calcining. Suitable radiations striking these metastable molecules change them to a critical state and under ordinary conditions when the sulfide is anhydrous they go back to the metastable condition with the emission of light. However, if the

[105] Roches claims to have discovered a process for doing this, but gives no details.

[106] Z. angew. Chem. 1923, *36*, 293; J. Chem. Soc. 1923, *124*, *ii*, 491.

[107] Chem. Zeit. 1922, *46*, 910.

[108] Compt. rend. 1923, *177*, 313; Chem. Abs. 1923, *17*, 3837.

sulfide is hygroscopic, hydrolysis results with the formation of hydrogen sulfide and zinc hydroxide. During the exposure a critical molecule of sulfide acts on the hydroxide likewise sensitized by light. Instead of returning to the metastable state the sulfide reduces the hydroxide, giving zinc and sulfurous acid. The latter reacts with hydrogen sulfide, giving water, sulfur and $H_2S_5O_6$.

Schleede, Herter and Kordatzki [109] also find that no blackening is shown by precipitated zinc sulfide unless it is first ignited. The presence of halogens, especially in conjunction with heavy metals, increases the sensitivity to light of the ignited material.

In order to form some qualitative idea as to the effectiveness of the different spectral regions in producing darkening Pfund [110] carried out the following ingenious experiments. A sample of light-sensitive lithopone was rubbed down in water and covered with a quartz plate. This specimen was then mounted in the focal plane of a quartz spectrograph so that the entire spectrum from an iron arc was projected upon the lithopone surface. In other words, the lithopone surface functioned as a photographic plate and indicated the regions of greatest light sensitiveness by darkening in these particular spectral regions. The darkened sample was then quickly photographed and thus a permanent record was obtained. It was found that wave-lengths greater than 3200 Å show very little darkening.

In order to establish a relation between darkening and the wave-length of the incident light, it is necessary to eliminate the variations in energy carried by the light of different wave-lengths. This is accomplished by means of a quartz monochromator, through whose ocular slit a beam of nearly monochromatic light is allowed to fall upon the blackened junction of a vacuum thermopile connected to a sensitive galvanometer. Since the galvanometer deflections are proportional to the incident energy only and independent of wave-length, a standard energy of incident light is realized. This is the so-called method of "equal energies." Having established this standard energy for a given wave-length, a sample of lithopone, rubbed down in water and covered by a quartz plate, is substituted for the thermopile behind the ocular slit and the time necessary for the appearance of the first visible darkening is recorded. This procedure is repeated for the various wave-lengths. The reciprocals of the number of seconds required to produce noticeable darkening, when plotted against wave-length, yield the desired "sensitivity."

The improvements which have been made in the light stability of lithopone are quite remarkable. A standardized test apparatus for determining the light stability of lithopones has been devised by Eastlack, who employs as a source of light the type of iron arc [111] developed by Pfund for spectroscopic research. Light stability may be measured in terms of the time of exposure necessary for the first darkening. The following table presents a series of typical results.

[109] Z. Physik. Chem. 1923, *106*, 386.
[110] Proc. Am. Soc. Testing Materials, 1923, *23*, ii, 375.
[111] Astrophysical Journal, 1908, *27*, 296.

	Light Stability Seconds Exposure	*Remarks*
Lithopone *A*	4	Old process lithopone
Lithopone *B*	35	New process lithopone
Lithopone *C*	135	New process lithopone

For additional data on the effect of ultraviolet on lithopone see Chapter 15, page 324.

Chapter 8.

Photochemical and Photolytic Reactions.

Organic Compounds.

The action of ultraviolet light on organic compounds depends largely upon the wave-length. Generally speaking the shorter the wave-length the more fundamental and deep-seated is the decomposition effected. Radiations of long and moderate wave-length very often produce polymerization or rearrangement, while compounds of a simpler structure are formed from the splitting up of more complex molecules as the short ultraviolet is approached. The final stage is reached with the production of carbon dioxide, methane, hydrogen and water.

Reactions facilitated by ultraviolet radiations are not always decompositions. Oxidation and reduction reactions, and various synthetic reactions are often catalyzed. (See also Chapter 11, Photosynthesis.)

In general, light favors endothermic reactions.[1] The decomposition of carbon dioxide into carbon monoxide and oxygen caused at ordinary temperatures by ultraviolet rays, is evidence of the powerful dissociating action of such radiation. This effect is important in the photochemical synthesis of carbohydrates. Hydrocarbons rayed with ultraviolet generally polymerize; e.g., acetylene yields benzene and a resinous substance. Alcohols, aldehydes and ketones decompose into carbon monoxide, hydrogen and hydrocarbons under some conditions. Ethers decompose like alcohols, but yield less hydrogen and more hydrocarbon. Acids may yield carbon dioxide and a hydrocarbon, with some carbon monoxide and hydrogen, probably due to preliminary reduction to aldehyde, but such drastic decomposition does not always take place. Dibasic acids readily lose carbon dioxide, leaving the monobasic acid. Keto acids react the same in ultraviolet as when heated. Esters yield carbon monoxide, carbon dioxide, hydrogen and a hydrocarbon or they may react similarly to the acids from which they are derived. Sugars react very much as with ferments. Bioses yield monoses; trioses a monose and a biose, which then yields two monoses. Monoses break up into carbon monoxide, methane and hydrogen. Some relation is to be expected between the absorption spectrum of a substance and its photochemical activity. According to Henri and Wurmser, the latter depends solely on that part of the absorption spectrum coinciding with the atomic groups affected by photochemical action. The rest of the light energy absorbed appears as heat. This gives the possibility that photochemical decomposition may differ with different wave-lengths, depending on the

[1] Gerretsen, Chem. Weekblad. 1916, *13*, 220.

groups responsible for absorption. Thus Bielecki and Henri were able to break up the absorption curves of aldehydes and ketones into simple elementary curves. Aldehydes gave two and ketones three curves. They conclude that rays of different wave-lengths are absorbed by different groups.

Photochemical oxidations and reductions are either equilibriums affected by light, or complete decompositions. The temperature coefficient is always low. The solvent has some influence; thus, chloroform in benzene, carbon tetrachloride, or ethyl acetate solution is oxidized by ultraviolet to chlorine, carbon monoxide and water, but not in carbon disulfide, ethyl ether, ethyl alcohol or acetone solution. Many substances such as mercury chloride, iron chloride, iron nitrate, uranyl salts, oxides of iron, manganese and cobalt, etc., act as catalyzers of photochemical oxidations.

Photochemical polymerization, condensation and isomerization occurs in many cases. Ketones and aldehydes are especially susceptible to photochemical condensation. Many photochemical isomerizations are equilibriums which can be changed by changing the wave-length. Those which reverse in the dark, Marckwald calls phototropic. In general, rays of high wave-length change the labile to the stable form; ultraviolet rays have the opposite effect. Photochemical hydrolysis is also very common; thus, most esters are saponified by water under the influence of the rays. The field of organic photochemistry, aside from its general significance, is very important in the study of structure.

Hydrocarbons, and their simple derivatives, are very often polymerized by exposure to ultraviolet radiation. Some of those possessing the more complex configurations undergo transformation into stereoisomers. Substituents frequently influence the course of the reaction, and are sometimes split off, or take part in side reactions. When oxidizing or reducing agents are present, these sometimes enter into the reaction.

It is stated by Urbain and Scal [2] that on exposure to ultraviolet rays of saturated liquid hydrocarbons, there is a liberation of acetylene, ethylene and hydrogen, and a decomposition of carbon. With pinene, the same products are obtained, and at the same time there is a marked formation of isoprene in the liquid.

Berthelot and Gaudechon [3] have investigated the action of the ultraviolet rays on a number of typical aromatic compounds. In no case was there observed an evolution of gas or any evidence of decomposition. The addition of uranium salts had no effect. A similar ability to resist decomposition was found in the case of other cyclic compounds (pyrrole, furfural, pyridine), and a few alkaloids. This behavior corresponds with the well known stability of the aromatic nucleus towards heat, light and chemical reagents. In the case of hexahydrobenzene and piperidine where the double bonds have disappeared decomposition took place, the latter compound evolving hydrogen. When the nucleus is attached to a straight chain that portion of the compound is attacked.

[2] Compt. rend. 1919, *168*, 887.
[3] Compt. rend. *152*, 376.

Berthelot[4] found benzene to remain unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combined with oxygen, yielding resinous products, if placed over mercury. A brown sediment, which is derived from the thiophene present in the hydrocarbon, forms at the junction of the liquids.

The fact that the most easily isolable products of the auto-oxidation in light, of benzene homologues, are carboxy-acids, is attributed by Suida[5] to the relative instability of the intermediate products. The most satisfactory source of radiation is a quartz lamp, used at a distance of about 10 centimeters from the specimen of substance. The velocity of the first stage of the oxidation can be approximately measured by the amount of peroxide formation; this is estimated by the action on a solution of potassium iodide, acidified with dilute sulfuric acid, with titration of the liberated iodine some hours afterwards. The parallel formation of carboxylic acids was estimated previously by titration with N/30-potassium hydroxide solution. It appears that the amount of acid formed cannot be entirely due to the decomposition of the peroxide.

The results indicate that pure benzene is practically passive but that the presence of thiophen causes peroxide formation. Methyl substituted benzenes undergo autoxidation when irradiated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes. The oxidation of xylene occurs more than twice as rapidly as that of the toluenes, and para-xylene oxidizes more rapidly than the ortho-isomer. The oxidation of 4-nitro-m-xylene under the influence of light resembles that of para-nitrotoluene, but is feebler.

Kailan[6] exposed toluene in the dark for about two years to the action of the radiation from a preparation containing 0.080 gram of radium in a glass envelope one millimeter in thickness, and found that less than 0.25 per cent of the toluene had been changed. The products formed included benzaldehyde, benzoic acid, and apparently formic acid. The increase in the density of the toluene and the weight of the residue left on evaporation indicate that the principal product of the reaction consists, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde. Changes of a similar nature and order of magnitude are produced in toluene when exposed for 22 hours to the radiation from a quartz mercury lamp at a distance of 8 to 9 centimeters. The action of the radium radiation on toluene in the presence of water yields three times as much acid as in the absence of water; benzoic and formic acids being produced, together with a non-acid residue. As regards the action on toluene of the radiation from a quartz mercury lamp, this is not increased by the presence of water to the same extent as the action of radium radiation, but oxalic acid is then produced, along with the benzoic and formic acids. Downs[7] claims that if a solution of

[4] Ann. Chim. Phys. 1900 (vii), *19*, 150.
[5] Monatsh. 1912, *33*, 1255.
[6] Monatsh. 1920, *40*, 445; J. Chem. Soc. 1920, *118*, i, 538.
[7] U. S. Patent 1,303,639.

crude anthracene in benzene, toluene or coal-tar naphtha is treated with ultraviolet rays, polymerization of the anthracene occurs and para-anthracene or di-anthracene is thrown down as a precipitate. The carbazole, phenanthrene and most of the other compounds originally present in the anthracene as impurities are unaffected by the ultraviolet rays and remain in solution. The para-anthracene is filtered off and may be reconverted into anthracene by sublimation. By this method a product of 95 per cent purity or higher may be obtained from a crude anthracene. According to Luther and Weigert [8] when a boiling solution of anthracene in phenetole is exposed to an arc lamp, dianthracene (melting point 270-280°) is formed in considerable quantity. On the other hand, when dianthracene is suspended for about 20 hours in boiling phenetole, light being excluded, it is transformed completely into anthracene and is dissolved. Similar results are obtained in boiling anisole and boiling xylene. The conversion of dianthracene into anthracene when dissolved in phenetole or anisole has been studied quantitatively and found to conform to the equation for a unimolecular reaction.

The application of ultraviolet rays in the analysis of gases is suggested by Landau.[9] Ethylene is slowly polymerized by radiation from a mercury lamp of 110 volts, but the action is incomplete even after 134 hours. With a 500-volt mercury lamp, polymerization is complete, both for ethylene and acetylene. Ethane and methane are not affected by ultraviolet, but in the presence of excess of oxygen the former is eventually completely oxidized to carbon dioxide and water. Landau suggests that the analysis of mixtures of hydrogen, ethylene, and ethane might be accomplished by the use of the ultraviolet.

Klever [10] notes that ultraviolet rays, sulfuric acid, and potassium bisulfate have a polymerizing effect on ethylene, while hydrochloric acid does not act in this manner.

By the action of ultraviolet rays on a mixture of ethylene and oxygen some formic acid is produced.[11]

Ferrer [12] reports that diphenylene ethylene $(C_6H_4)_2C:CH_2$ is stable for several hours in the dark, but is completely polymerized and rendered insoluble in ether, when exposed for 10 minutes to the mercury arc.

According to Kaufmann [13] trans- and cis-αβ-di-iodoethylene and αα di-iodoethylene are decomposed with liberation of iodine when their ethereal solutions are exposed to ultraviolet, the velocity of the reaction in the case of the compound first named being approximately twice as great as that in the remaining two cases.

Vinyl chloride, $CH_2:CHCl$, and vinyl bromide, $CH_2:CHBr$ polymerize rapidly when exposed to light. The chloride forms an

[8] Sitzungsber. K. Akad. Wiss. Berlin, 1904, 828; J. Chem. Soc. 1904, *86*, ii, 463.

[9] Compt. rend. 1912, *155*, 403; J. Chem. Soc. 1912, *102*, *ii*, 986.

[10] Mitt. Chem.-tech. Inst. Tech. Hochschule Karlsruhe 1923, No. 1, 1; Chem. Abs. 1924, *18*, 1976.

[11] Compt. rend 1910, *150*, 1327. Acetylene behaves similarly.

[12] Anales soc. españ. fís quím. 1922, *20*, 459; Chem. Abs. 1923, *17*, 3177.

[13] Ber. 1922, *55*, 249.

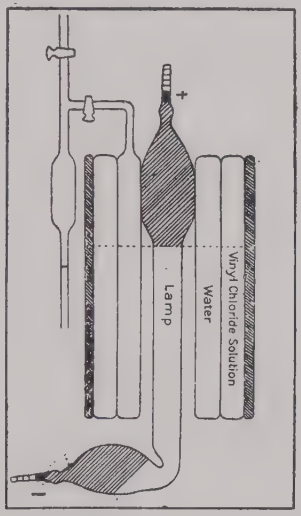
amorphous insoluble substance of specific gravity 1.406, which melts above 130° C. with decomposition.[14] The polymerized bromide is likewise insoluble in water, alcohol or ether, and has a specific gravity of 2.075. The polymer begins to decompose at 125°-130° C. It is stated by Plotnikov[15] that a solution of vinyl chloride, as distinguished from ethylene, polymerizes to a substance thought to be $(CH_2:CHCl)_{16}$ in the extreme ultraviolet of a mercury lamp. Sunlight is effective only in the presence of catalyzers, such as the salts of manganese, cobalt, nickel, copper and vanadium, and is most active with uranyl salts. The white precipitate obtained dissolves in many organic solvents to form colloidal solutions varying in character from paste to solid. Details of the production of useful products by the polymerization of vinyl esters when employing the mercury vapor lamp are given by Klatte and Tollett.[16] The polymerization can be accelerated by catalyzers, benzoyl peroxide, ozonides, and anhydrides of organic acids in conjunction with an agent giving off oxygen (perborates, percarbonates, silver oxide, etc., being mentioned for the purpose).

The polymerization products, which form more or less rapidly in accordance with the intensity of illumination and the temperature, are solid, colorless and transparent celluloid-like masses which are odorless and can be turned, cut, planed, and otherwise manipulated to form various articles. These solids rendered plastic in hot water can be molded and, upon cooling, the material becomes hard again. Chlorinated esters may be polymerized by heat and light as a two-stage operation in the following manner: 1 kilogram of vinyl chloroacetate is mixed with from 0.5 to 1 gram of benzoyl peroxide and carefully heated in a large vessel provided with a reflux condenser. At from 80° to 100° polymerization takes place, while the temperature rises rapidly. At this time care should be taken to cool the reaction vessel. The violence of the reaction may be modified by diluting the reaction liquid with an indifferent solvent; for instance, in the present example, about 300 grams of chlorobenzene can be used. The reaction product is a viscous syrupy mass which can be further treated by exposing to light without a diluent, solid masses being obtained as the remaining unaltered vinyl ester polymerizes. The syrupy solution or a solution made from the completely polymerized ester may be used as a lacquer or other coating compound. When allowed to dry in thin layers, colorless films of a celluloid-like nature are said to be obtained. Vinyl chloride may be polymerized by ultraviolet rays, but the product derived is not as satisfactory as that obtained from the esters mentioned. According to Kuhl[17] the polymerization of vinyl esters (vinyl acetate or vinyl chloroacetate) by ultraviolet light yields solid masses which may serve as substitutes for celluloid and which are fireproof and odorless. The polymerization if assisted by catalytic agents (organic peroxides) to give thick syrups which on illumination give solid masses having valuable properties.

The polymerization of vinyl chloride in the extreme ultraviolet has been utilized by Plotnikow to make "synthetic rubber" (Zeitsch. f. wiss. Phot. 1922, *21*, 117; India Rubber World 1925, *71*, 280). He exposed a 2½ per cent solution of vinyl chloride in methyl alcohol to ultraviolet radiation. The apparatus used by Plotnikow is shown in Figure 46. Carbon tetrachloride was found to accelerate the transformation.

[14] Baumann, Annalen *163*, 317.
[15] Z. wiss. Phot. 1922, *21*, 117.
[16] U. S. Patent 1,241,738, Oct. 2, 1917.
[17] Reports of the Progress of Applied Chemistry issued by the Society of Chemical Industry, 1916, *1*, 192; J. S. C. I. 1915, *34*, 623.

As a representative of the β, γ, ethylenic acids, γ phenylvinylacetic acid in benzene solution was exposed to ultraviolet rays by Stoermer and Stockmann.[18] The acid resinified to a considerable degree. Although the allo-form could not be obtained in crystalline form, the crystalline allo-amide was isolated and converted by raying into the stable variety. Ostromuislenski [19] obtained by the polymerization of vinyl bromide a material which he termed caouprene bromide. This



Courtesy India Rubber World.

FIG. 46.—Apparatus for Synthesizing "Rubber" from Vinyl Chloride. A Water-cooled Jacket prevents overheating of the Vinyl Chloride Solution.

exists in three forms, α, β and γ. When the α and β forms are submitted to the action of ultraviolet the γ form is yielded. Stobbe and Toepfer [20] report that p-vinylanisole is polymerized when placed in glass tubes in direct sunlight, the extent of reaction being about the same after four days' exposure as after four hours at 100° C. in the dark. If a little of the polymeric form is added, the polymerization proceeds as far in one day as it does in four days with the pure substance. When p-vinylanisole in quartz tubes at 30° C. is alternately irradiated by a quartz mercury lamp and kept dark, polymerization appears not to proceed during the period of raying, but during the following periods of darkness. It is concluded that rays of wave-length longer than 330 μμ (3300 Å) cause polymerization while rays of shorter wave-length reverse the reaction.

According to Berthelot and Gaudechon [21] exposure of acetylene to

[18] Ber. 1914, *47*, 1793.
[19] J. Russ. Phys. Chem. Soc. 1912, *44*, 204.
[20] Ber. 1924, *57 B*, 484; Chem. Abs. 1924, *18*, 2503.
[21] Compt. rend. 1910, *150*, 1169; J. Chem. Soc. 1910, *98*, *i*, 349.

the action of ultraviolet rays brings about partial polymerization of the gas, without decomposition and without formation of benzene. The product of polymerization is a yellow solid, and the residual gas is pure acetylene. Under the same conditions, ethylene polymerizes to a liquid having an odor of rancid fat, boiling point below 100°. The product resembles the mixture containing acetylene, produced in the pyrogenic decomposition of waxes. Cyanogen is transformed into para-cyanogen under the influence of ultraviolet. The presence of hydrogen or nitrogen with the acetylene does not modify the action, and mixtures of acetylene with ethylene or cyanogen give simple mixtures of the foregoing products.[22] Mathews and Dewey [23] also find that acetylene is converted, on exposure to ultraviolet radiation, into a solid polymer rather than into benzene.

In photochemical reactions with ethylenic and acetylenic compounds in presence of oxygen, the double and triple linkages are ruptured and simple acids formed, while in presence of ammonia cyclic compounds are formed. Ethylene, for example, yields first amino-ethylenes and then ring formation takes place with production of compounds of the pyrrolidine and pyridine types, which may be regarded as the mother substances of alkaloids. In the case of aqueous solutions, the water also is decomposed to a small extent. According to a process described by Heinemann [24] the union of acetylene and methane is effected by heating these gases in the presence of catalytic metals, such as iron, nickel, copper, silver, platinum, iridium and palladium. Instead of using heat, the reaction in the presence of catalytic metals may be effected through the agency of ultraviolet or other chemically active rays. For example, pumice stone, provided with a coating of copper, is dipped in a solution of chloride of platinum, and is dried. The salt is then reduced. In this way there is obtained a contact body consisting of two metals which are stated to exert a mutual balancing effect on one another, the more active property of the platinum group metal being mitigated by the less active property of the other metal associated therewith, and allowing the desired reaction to take place at a moderate temperature. A mixture of equal volumes of acetylene and methane is passed into a reaction tube containing the catalyst. During the passage of the mixture through the tube the reaction space is subjected to the influence of chemically active rays. When ultraviolet rays are used a number of mercury lamps are supported in close proximity to the reaction tube. Matthews and Elder [25] produce compounds of sulfur dioxide and unsaturated hydrocarbons by direct combination by exposing the mixed liquids to sunlight or ultraviolet rays, or in some cases by heating. The examples given are the compounds with pseudo-butylene $(C_4H_8SO_2)_n$, propylene, amylene and ethylene. The butylene product is a horny or glassy, clear white solid, soluble in chloroform or tetrachlorethane and not easily

[22] See also Berthelot and Gaudechon, Compt. rend. 1912, *155*, 521; J. Chem. Soc. 1912, *102*, *i*, 741.

[23] Compt. rend. 1910, *151*, 395.

[24] U. S. Patents 1,202,385, Oct. 24, 1916, and 1,134,667, April 6, 1915.

[25] British Patent 11,635, May 11, 1914.

inflammable. It can be used for making varnishes, transparent films, etc., and may be mixed with celluloid by first softening both with acetone. It renders the celluloid less inflammable. Dedichen and Halse [26] expose raw turpentine oil to the action of ultraviolet rays while subjecting it to the action of air or oxygen. The oil is then treated with iron chloride to refine and deodorize it and obtain a mixture of α and β-pinenes containing dextro-rotary β-pinenes.

Stobbe [27] claims that styrene has never been completely transformed spontaneously into pure metastyrene, indicating that equilibrium is established between the polymerizing and depolymerizing reaction in such a homogeneous system. Five per cent solutions of styrene and metastyrene showed the following change in refractive index after 0, 20, 32, 95 and 230 hours raying in uviol tubes: styrene, 1.49883, 1.49911, 1.49939, 1.4994, 1.4994; metastyrene: 1.50125, 1.50125, 1.50125, 1.50116, 1.50116. The irradiated solution of styrene gave a precipitate of metastyrene with alcohol; that of metastyrene decolorized permanganate; while the solutions kept in the dark did not. Similar experiments with stilbene in benzene indicate that the equilibrium of stilbene lies very far toward the right, while in alcohol, ether, chloroform, trichlorethylene and pyridine there is apparently no polymerization. Stoermer and Oehlert [28] describe a series of attempts to convert stable into labile stilbene derivatives by the action of ultraviolet. In general, experiments are greatly complicated by the formation of resinous products, and the yields are not good. In all the cases investigated the melting points of the labile are lower than those of the corresponding stable compounds, and the isomerides are not infrequently distinguished by marked differences in color. 2:4-Dinitrostilbene, $C_6H_5CH:CH.C_6H_3(NO_2)_2$, is converted by exposure in benzene solution to the rays of a quartz mercury lamp to the extent of 20 per cent into allo-2:4-dinitrostilbene.

In ultraviolet radiation indene resinifies, apparently by polymerization.[29] Stobbe and Färber [30] have carried out a series of experiments on the photo-polymerization of pure indene.

Investigations by Stobbe and Schmitt [31] show that alkyl iodides, either pure or in solution, do not become colored when preserved in the dark for two and a half months, but in daylight a coloration is produced in a few hours in all cases. This coloration, however, does not occur if oxygen is absent. The action of ultraviolet on solutions of ethyl iodide, methyl iodide, n-propyl iodide, and isopropyl iodide in benzene and ethyl alcohol has been studied. It was found that a solution of iodine in benzene or chloroform, after illumination for twenty hours with a quartz mercury lamp, on dilution gave a yellow solution, and not

[26] U. S. Patent 1,253,793, Jan. 15, 1918.
[27] Ber. 1914, *47*, 2701.
[28] Ber. 1922, *55 B*, 1232.
[29] Guntz and Minguin, Compt. rend. 1911, *152*, 373; note Weger and Billmann, Ber. 1903, *36*, 642; also Ciamician and Silber, Ber. 1913, *46*, 420.
[30] Ber. 1924, *57*, 1843.
[31] Zeitsch. wiss. Photochem. 1920, *20*, 57.

a red solution, as untreated iodine solutions do. Experiments show that the decomposition of alkyl iodides with the liberation of iodine is an oxidation. Ethyl, methyl, and n-propyl iodides are similar in their behavior toward radiation, but isopropyl iodide is much less stable. Ethyl bromide is decomposed by ultraviolet of short wave-length with the liberation of bromine. Solutions of iodine in alcohols pass, in the course of time, into solutions of periodides (hydrogen tri-iodide or other additive compounds). This reaction is accelerated by light or spongy platinum. The absorption spectrum of true solutions of iodine consists of a single absorption band in the visible part of the spectrum, the position of which is independent of the nature of the solvent. The more the absorption is displaced toward the violet end of the spectrum the greater is the heat of solution of iodine in the solvent. When such solutions are diluted with several volumes of benzene or chloroform, the color immediately becomes red. The spectrum of the periodide solutions shows two absorption bands in the ultraviolet with frequencies 280 and 345 μμ (2800 and 3450 Å) and on dilution with benzene or chloroform yellow solutions are obtained. During the change of iodine into the periodide, solutions of mixtures are formed which show three absorption bands. The spectra of iodine described by various observers indicate that from 5 per cent to 100 per cent of the iodine present had been converted into periodide. Dimethylpyrone iodide exhibits the same spectrum as the periodide.

From studies of the photolysis of organic iodides, Job and Emschwiller[32] find that the action of light on ethyl iodide in a closed system and in complete absence of oxygen results in the liberation of iodine and of a large quantity of gas composed principally of ethylene and ethane, together with small amounts of butane and hydrogen. The presence of butane is readily explained by the assumption of a unimolecular decomposition, and that of ethylene and ethane, which is often observed when an ethyl radical is set free, is attributed by Schlubach and Goes[33] to a lack of equilibrium in the ethyl radical which causes migration of one of its hydrogen atoms to a neighboring radical. Since, however, ethylenic hydrocarbons are never found in the gas resulting from the photochemical decomposition of alcohols, aldehydes, acids, or ketones, the iodine from the ethyl iodide probably acts as acceptor towards a hydrogen atom of the ethyl radical, ethylene and hydrogen iodide being first formed and the latter then being decomposed under the influence of light. Results similar to the above are observed with methyl iodide. If the iodine in ethyl iodide is represented as united to the carbon by means of a co-valence, the quantum of luminous energy which detaches the iodine from the molecule must bring the latter to an energy level at least equal to the critical level. If it touches and just suffices to bring to the critical level an average molecule, this quantum, $h\nu$, will by definition be the critical complement and measures the energy of linking of the co-valence, C — I. When a tube containing ethyl iodide is placed in the spectrum of the carbon arc, the reaction appears distinctly as soon as wave-lengths shorter than 410 μμ (4100 Å) are reached and increases in intensity as the frequency increases.[34] The energy quantum corresponding with this wave-length is 69,300 cals. per g.-mol., which is thus approximately the energy of the carbon-iodine co-valence in ethyl iodide.

[32] Compt. rend. 1924, *179*, 52.
[33] J. Chem. Soc. 1922, *122*, *i*, 1204.
[34] Cf. Crymble, Stewart, and Wright, J. Chem. Soc. 1910, *98*, *ii*, 470.

According to Maynard [35] the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If mercurous iodide is used with methyl iodide, methyl mercuric iodide is formed rapidly. The action of metallic mercury is confined almost entirely to methyl iodide. The use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide.

Carbon disulfide in admixture with argon undergoes a partial decomposition when exposed to bright sunlight and the sides of the containing vessel become coated with a brown deposit; [36] when exposed to diffused light, it remains unaltered, and does not react with hydrogen or argon. When a mixture of argon and gaseous carbon disulfide is submitted to the action of the silent discharge for 3 months in diffused light, the electrodes being maintained at a difference of potential of 200 volts, the former gas remains unaltered, while 60 per cent of the latter is converted into yellow, resinous products. Bruhat and Pauthenier [37] have observed the decomposition of carbon disulfide by ultraviolet rays. When this substance is exposed in quartz cells to the quartz mercury arc, a deposit of sulfur is formed on the walls. In order to fix the sulfur the interior of the cells was coated with a thin film of silver, which is transparent to the ultraviolet. For a 6-hour exposure, the long wave limit of decomposition was found to be 366 μμ (3660 Å). The fact that carbon disulfide is practically non-absorbent for this wave-length is probably due to liberation of sulfur atoms at a considerable depth in the solution and subsequent fixation of the silver atoms to give brown silver sulfide at a short distance from the place of decomposition.

Compounds containing oxygen such as alcohols, aldehydes and ketones are very generally decomposed by ultraviolet, under proper conditions. The decomposition products in many cases undergo secondary reactions. Polymerization and rearrangement also characterize the behavior of some members of these classes.

Henri and Ranc [38] by subjecting a 10 per cent aqueous solution of glycerol for 6 hours to the action of ultraviolet radiation from a 500-volt quartz mercury lamp, have shown that the glycerol molecule is decomposed with the production of formaldehyde and acids as well as other aldehydic substances. The decomposition is considerably increased by the presence of hydrogen peroxide, the activation being proportional to the quantity of peroxide added.[39] Bierry, Henri and Ranc [40] previously carried out experiments on the action of ultraviolet

[35] Science 1922, *56*, 492.

[36] Berthelot, Ann. Chim. Phys. 1900 (vii), *19*, 150.

[37] Compt. rend. 1924, *178*, 1536. Determinations of the refractive index of carbon disulfide have been made by Bruhat and Pauthenier as far as 2537 Å. in the ultraviolet, with special attention to the neighborhood of the absorption band at 3220 Å. Compt. rend. 1925, *180*, 1018.

[38] Compt. rend. 1912, *154*, 1261.

[39] The decomposition takes place more readily in the presence of water.

[40] Compt. rend. 1911, *152*, 535.

on glycerol. Two mercury lamps in parallel served as the source of light. The liquids were placed in quartz flasks or in large open porcelain basins. The experiments were made at different temperatures, in presence of air or in vacuum, and with or without shaking, and the concentration of the glycerol solution was varied from 1 to 100 per cent. After treatment the solutions were concentrated in a vacuum and their behavior studied towards Fehling's solution and phenylhydrazine. The action on neutral glycerol at 25° C. in the presence of air leads to the formation of a glycerose giving a positive phloroglucinol reaction for glyceric aldehyde. The quantity is small and other substances reacting with phenylhydrazine are also formed. In the presence of alkali the product is not glycerose but β-acrose which was identified by means of the phenylosazone. The amount formed is small, but it may be increased by the addition of salts of iron or cobalt or in particular by uranium salts. Numerous other compounds are also formed.

Henri[41] has measured the refractive indices of methyl, ethyl, propyl, butyl, amyl and heptyl alcohols, of glycol and of pentane, hexane, heptane and cyclohexane for rays of wave-length $\lambda = 420\text{-}215$ μμ (4200-2150 Å) and from his results has calculated the molecular refractive powers for CH_2 and H and O of the hydroxyl group. Up to $\lambda = 260$ μμ (2600 Å) the refractive power of CH is perfectly additive, as in the visible spectrum, while for rays of shorter wave-length the additivity is only a first approximation.

Although terephthalaldehyde is very stable in the solid state and in solution in benzene in the dark, Suida[42] finds that its solution undergoes rapid atmospheric oxidation when rayed by a mercury lamp, and a white crystalline deposit is formed. The deposit consists of terephthalaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid. The solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution. This oxidation of terephthalaldehyde appears not to occur at all if light is excluded, and it is not accelerated by the presence of nitrobenzene, in fact this substance exerts a hindering effect. A comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthalaldehyde is considerably diminished by the presence of a similar group in the para-position. By interposing solutions of potassium chromate and of quinine sulfate between the solution and the source of light, it is discovered that the effect is mainly due to the ultraviolet rays, but that yellow and red light can cause the oxidation to occur, although only very feebly. Spectrographic examination indicates that the effective rays are from 400 to 300 μμ (4000 to 3000 Å).

According to Weigert and Kummerer[43] the transformation of o-nitrobenzaldehyde into o-nitrosobenzoic acid under the influence of light is independent of air and is a simple case of isomeric reaction. In order to study the process quantitatively, acetone was selected as a

[41] Compt. rend. 1914, *158*, 1892.
[42] Monatsh. 1912, *33*, 1173; J. Chem. Soc. 1913, *104*, *i*, 52.
[43] Ber. 1913, *46*, 1207.

solvent, since the acid would be esterified by alcohol, and is only sparingly soluble in other media. The solutions were exposed in glass troughs to the rays from a quartz mercury lamp and protected from heat rays by a tank of running water, and as occasion required, filters of nitrosodimethylaniline in 0.0017 per cent solution, and quinine sulfate in 0.05 per cent solution were interposed to cut off the violet, blue and ultraviolet rays respectively. Preliminary experiments showed that the same results were obtained under the same conditions, that it was unnecessary to stir the solutions, and that the amount of transformation was practically proportional to the time of irradiation. In order to study the influence of the intensity of the light, the lamp was stopped down so as to bring the source of the rays approximately to a point, and the solutions were placed at such distances that the intensities were in the ratio 4:2:1, and then rayed for periods which varied as 1:2:4. It was found that slightly less transformation had occurred in the most remote vessel, thus showing that the Bunsen-Roscoe law, that the same quantity of light produces the same chemical effects, is not quite admissible. In further experiments on the influence of the initial concentration of the solution, the light was filtered through the quinine sulfate or nitrosodimethylaniline solutions, when, after allowing for the amount of light absorbed by these filters, it was found that the sum of the quantities of o-nitrosobenzoic acid formed was practically equal to the amount produced, under otherwise similar conditions, by unfiltered light. In the case of ultraviolet, the effect is independent of the concentration, but for violet light the speed of transformation is, at first, proportional to the concentration. The order of the reaction therefore changes with the kind of light, so that no simple law can be deduced to express the quantitative course of the reaction. No proportion existed either between the speed of the reaction and the amount of light absorbed by the aldehyde although the increase was in the same direction. With mixed light, the chief work is done in dilute solutions by the ultraviolet rays, and in concentrated solutions by the violet. Hartley and Scott [44] also studied the photochemical change of o-nitrobenzaldehyde into o-nitrosobenzoic acid, as well as the change of cinnamylidenemalonic acid into what is probably diphenyltetramethylenediethyldicarboxylic acid. It appears that one quantum is absorbed for each molecule transformed.

According to Jorissen and Ringer [45] when a mixture of benzaldehyde (1 molecule) and acetic anhydride (2 molecules) with or without admixture of sand is exposed in diffused light and in a closed vessel to an atmosphere of oxygen, benzoyl acetyl peroxide is obtained. The light from a Welsbach burner is inactive, but the electric arc is extraordinarily active, a marked after effect, but no period of induction, being noticed. When passed through a red glass plate, the electric light is inactive, but when passed through a violet plate is still active, showing both a period of induction and after effect. Magnesium light similarly accelerates the oxidation with a short period of induction and

[44] J. Chem. Soc. 1924, *125*, 1233; Chem. Abs. 1924, *18*, 3548.
[45] Chem. Centr. 1905, *76*, i, 817; Chem. Weekblad. *2*, 19.

more prolonged after effect. Röntgen and radium rays are inactive. In endeavoring to oxidize benzaldehyde in the presence of oxygen, directly to benzoyl hydroperoxide, Suida [46] used a Heræus quartz lamp. A current of oxygen was passed through benzaldehyde in petroleum ether and the solution was exposed at a distance of about two centimeters from the lamp. The vessel in which the benzaldehyde was exposed was cooled with ice. During an exposure of 6 hours a considerable quantity of benzoic acid formed, together with small quantities of a peroxide body. On cooling the vessel by means of solid carbon dioxide and ether the formation of the peroxide was much increased. A white deposit was slowly obtained which had strong oxidizing properties and a pungent odor. The peroxide substance could not be isolated readily on account of rapid conversion into benzoic acid. At the same temperature, but with the exclusion of light, there was no indication of formation of the peroxide body.

Benzaldehydephenylhydrazone does not redden at all, even on prolonged exposure to the air, if light is excluded.[47] In light, its color alters in a remarkable way. In diffused light, reddening takes place slowly, but in sunlight, the change becomes very noticeable in a few minutes and the color quickly deepens until after a few hours a maximum intensity is reached, when the crystals have a brilliant scarlet color resembling that of azobenzene. The light from an electric arc playing between iron poles (which is extremely rich in ultraviolet rays) also brings about the change, the velocity of which falls off in the ordinary way as the distance from the arc is increased. Exposed in a quartz tube at a distance of five centimeters the change was about as rapid as in direct winter sunlight. The transformation, however, appears not to be due to ultraviolet rays, as its rate is not affected by interposing a sheet of ordinary crown glass. Jorissen and Vollgraff [48] claim the autoxidation of benzaldehyde and of pinene under the influence of the rays from a uviol lamp increases the electric conductivity of oxygen.

Davies [49] notes that 5-nitro-2-methoxy-3-ethoxybenzaldehyde undergoes no change of color or melting point when exposed in pure acetone solution for twenty-five hours to ultraviolet rays from a powerful mercury lamp. On the other hand, the well washed nitration product (melting point 85° C.) obtained by precipitation with water rapidly becomes greenish-blue when exposed to ultraviolet rays under the same conditions.

Per-acids [50] are prepared by treating aldehydes with oxygen, or oxygen containing gases at low temperatures preferably with the exclusion of injurious impurities such as water and manganese compounds. The reaction is facilitated by the use of chemically active rays. Xylene mixed with an aromatic nitro-hydrocarbon is reported

[46] Ber. 1914, *47*, 471.
[47] Chattaway, J. Chem. Soc. 1906, *89*, 463.
[48] Chem. Weekblad 1915, *12*, 93; J. Chem. Soc. 1915, *108, ii*, 80.
[49] J. Chem. Soc. Trans. 1923, *123*, 1590.
[50] British Patent 16,849, July 22, 1913.

to contain more active oxygen after exposure to light and oxygen than pure xylene so treated, but Suida [51] found that the presence of a nitro-compound reduced the total yield of oxidation product although considerable quantities of toluic aldehyde were present. Thus in the presence of a nitro-hydrocarbon the less stable products of oxidation (aldehydes and peroxides) remained, while the pure chemical reaction (the decomposition of these primary products to the next higher and more stable stage of oxidation) was delayed. It was possible by cooling in carbon dioxide and ether to bring almost to a standstill the decomposition of the benzene hydroperoxide (formed from benzaldehyde by the action of ultraviolet). The product of the primary auto-oxidation process could not be isolated, as it decomposed into benzoic acid within a few minutes after removing it from the cooling mixture.

Moureu, Murat and Tampier [52] find that acrolein, when exposed to diffuse daylight in sealed tubes, is unchanged after two months. Winter sunlight solidifies about one-third of it in twelve days while in a quartz tube, radiation from a mercury vapor lamp completely solidifies it in one and one-half hours.[53]

A detailed study of the photolysis of acetaldehyde has been made by Berthelot and Gaudechon,[54] who state that ultraviolet rays of long wave-length do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid. The amount of acid produced is far greater when the aldehyde is in the form of vapor than when it is liquid. With rays of wave-length 250 μμ (2500 Å) polymerization is rapid, both para and meta acetaldehyde being formed. No resinification results from the action of long ultraviolet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerization and resinification, but favors acidification, formic acid being produced in this case and in amount almost equal to that of the acetic acid. Of three compounds studied, viz.: acetaldehyde, ethyl alcohol and acetic acid,[55] only acetaldehyde is decomposed by sunlight (wave-length greater than 300 μμ [3000 Å]). Rays from a mercury lamp screened by thin glass which absorbs all rays of wave-lengths less than 300 μμ (3000 Å) decompose acetaldehyde in accordance with the equation $CH_3 . CHO = CO + CH_4$. Frequently the proportion of methane to carbon monoxide actually found is somewhat less than corresponds to this equation, for the light causes polymerization of some of the aldehyde to paraldehyde which is then photolyzed to carbon monoxide and ethane or more complex substances. These latter reactions are most readily produced by the extreme ultraviolet rays. Direct rays from a mercury lamp, without any interposed screen,

[51] Ber. 1914, *47*, 467; Monats. Chem. 1912, *33*, 1268.
[52] Ann. chim. 1921, *15*, 221; Compt. rend. 1921, *172*, 1267; Chem. Abs. 1921, *15*, 2220; 1922, *16*, 55.
[53] Oxidation of acrolein in light, see Moureu, Dufraisse and Badoche, Bull. Soc. chim. 1924, *35*, 1572 and 1591.
[54] Compt. rend. 1913, *156*, 233.
[55] Compt. rend. 1913, *156*, 68.

photolyze not only acetaldehyde but ethyl alcohol and acetic acid. Ethyl alcohol is decomposed primarily into acetaldehyde and hydrogen,[56] but usually some carbon monoxide and ethane are formed by the further decomposition of the aldehyde. By the photolysis of acetic acid a gas was obtained which contained 44 per cent of carbon dioxide, 17 per cent of carbon monoxide and 39 per cent of combustible gases.[57] These results relate to photolysis in absence of air. In presence of water the reactions take substantially the same course, but there is a tendency toward the formation of acid products.

The same investigators [58] also give the results of analyses of mixed gases obtained by exposing a number of substances to a quartz mercury lamp. The compounds examined included the first three members of the aliphatic saturated alcohols, aldehydes, and acids, also formamide and diethyl ketone. Acetone is decomposed very rapidly by ultraviolet, giving carbon monoxide (49 volumes), methane (5 volumes), and ethane (46 volumes); in aqueous solution carbon dioxide is also formed. With sunlight the acetone is hydrated and decomposed, giving methane and acetic acid.[59]

Henry and Wurmser [60] exposed an aqueous solution of acetone to rays of wave-length 298.1-214.4 μμ (2981-2144 Å) and measured the rate of acid formation. Their results show that there is a striking similarity between the absorption curve of acetone in the ultraviolet portion of the spectrum and the chemical activity of the different rays. The law of photochemical absorption applies to the action of ultraviolet rays on acetone in aqueous solution, and the reaction is an example in which the extreme ultraviolet rays are less active than those of the greater wave-length.

Observations by Grossmann [61] on the absorption spectrum of ethyl acetoacetate show that it is decomposed by ultraviolet rays, yielding mainly ethyl acetate and acetic acid. Under the same conditions acetylacetone gives acetic acid and acetone.

From an investigation of diketones, Porter, Ramsperger and Steel [62] find that under the influence of ultraviolet radiation, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200° C. or above. In dilute alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin. In aqueous alcohol in contact with air it is converted into benzoic acid. Further oxidation of the benzoic acid gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in the presence of oxygen, were never found in the exposed benzil solutions.

[56] J. S. C. I. 1911, *30*, 1086.
[57] J. S. C. I. 1910, *29*, 1081.
[58] Compt. rend. 1910, *151*, 478; J. Chem. Soc. 1910, *98*, *ii*, 814.
[59] Compt. rend. 1910, *150*, 1164.
[60] Compt. rend. 1912, *155*, 503.
[61] Z. Physik. Chem. 1924, *109*, 305; Chem. Abs. 1925, *19*, 39.
[62] J. Am. Chem. Soc. 1923, *45*, 1827.

Under the influence of ultraviolet rays, diacetyl vapor yields ethane and carbon monoxide, and an aqueous solution of diacetyl yields acetic acid and acetaldehyde.

Boeseken and Coehn[63] studied the photochemical reduction of ketones by anhydrous alcohol, both by direct sunlight and rays from a quartz mercury arc lamp. Five grams of the ketone in 50 cubic centimeters of dry alcohol sealed in ordinary glass tubes were exposed. Reduction in this manner gave only pinacols. The reaction velocity is independent of the concentration of ketone and proportional to the concentration of the alcohol and may be represented as follows: 2 ketone + alcohol = pinacol + aldehyde. The temperature coefficient is very small. The rate of pinacol formation depends greatly on the alcohol employed, methyl alcohol and allyl alcohol acting slower than other primary and secondary alcohols. The rate also depends on the ketone, benzophenone being reduced more rapidly than other ketones. Many were not reduced at all. The relative rates in different alcohols are the same. The active light in the ketone reduction lies between 400 μμ and 430 μμ (4000 and 4300 Å) and probably at or near the rays 404.7 μμ and 407 μμ (4047 and 4070 Å). The relation of the rate of pinacol formation is the same in sunlight and in the mercury arc rays. When two ketones are present simultaneously, one absorbs a part of the rays needed by the other. This is also evident when the light, after passing through one, is allowed to act on another. The interference is greater than would be expected.

The effect of exposure to a mercury vapor lamp of a series of ketones dissolved in a great variety of anhydrous alcohols and a few other substances has been noted.[64] In all cases where reduction occurs not a trace of the hydrol is formed, the ketones being quantitatively changed to the pinacones. The addition of sodium ethoxide to the alcoholic solution results in the formation of the hydrols, as is to be expected. The conclusion is reached that in the reduction of aromatic ketones the hydrogen unites exclusively with the oxygen; the resulting half-pinacone polymerizes to the pinacone, and the latter, in the presence of hydroxyl ions is transformed into an equal molecular mixture of the ketone and the hydroxyl.

McGookin and Heilbron[65] find that exposure of an alcoholic solution of the yellow form of 2-hydroxystyrylmethyl ketone to rays of short wave-length from a quartz mercury vapor lamp for 24 hours results in complete transformation to the colorless form.

The photocatalytic influence of ketones on the velocity of oxidation of ethyl alcohol has been studied by Coehn.[66] This action is measured by the rapidity with which oxygen is absorbed in the reaction: alcohol + oxygen + ketone + light → ketone + acetaldehyde + water. The velocity of activation is inde-

[63] Wetenschappen 1914, *23*, 765; see also Coehn, Rec. trav. chim. 1920, *39*, 243; Chem. Abs. 1920, *14*, 2786.

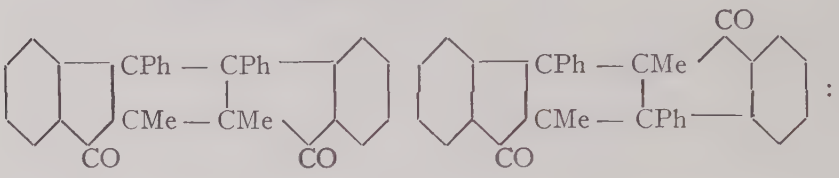
[64] Wetenschappen J. 1914, *17*, 849; J. Chem. Soc. 1915, *108*, *ii*, 37.

[65] J. Chem. Soc. 1924, *125*, 2102.

[66] Prod. Acad. Sci. Amsterdam, 1923, *26*, 443; Chem. Abs. 1921 *15*, 3617; 1924, *18*, 50. Boeseken, Rec. trav. Chim. 1921, *40*, 433.

pendent of the concentration of the ketone within wide limits. A diminution in the activity in very high ketone concentrations is attributed to mutual disturbances of the ketone molecules. That in lower concentrations is accounted for by the absence of a sufficient quantity of activatable ketone molecules, so that a part of the light is left unused. The aromatic nucleus is necessary for photoactivity of the α, β-diketones.

Under the influence of the ultraviolet rays emitted by a quartz mercury vapor lamp, 3-phenyl-2-methylindone in benzene solution gives rise to two diphenyldimethyltruxones,



(1) white crystals, melting point 307-308° C.; (2) pale canary-yellow prisms, melting point 259-260° C. These compounds react with concentrated sulfuric acid to form 3-phenyl-2-methylindone. When the latter is exposed in benzene solution to the action of ordinary sunlight, the truxone of melting point 307-308° C. is formed together with what appears to be a third isomeride, yellow crystals, melting point 174-176° C. 3-Phenol-2-methylindone oxime undergoes no change when exposed in benzene solution to ultraviolet radiation, but under similar conditions the phenylhydrazone yields a compound, red laminæ, melting point 73-75° C., which may possibly be the isophenylhydrazone. A third diphenyltruxone, $C_{30}H_{20}O_2$, yellow needles, melting point 184-185° C., is obtained when the colorless isomerides formed by treating ethyl ββ-diphenyl-lactate with concentrated sulfuric acid is exposed in benzene solution to ultraviolet rays.[67] DeFazi[68] exposed a benzol solution of α-methyl-β-phenylindone in a quartz tube to the ultraviolet radiation of a 1500-candle-power quartz mercury lamp placed 20 cm. from the container. Crystals began to separate after 24 hours' irradiation, and after seventy hours dimethyl-diphenyltruxone was filtered off. A substance which is probably an isomer of the truxone was also formed.

Bodforss[69] found that benzoylphenylethylene oxide, benzoyl-m-nitrophenylethylene oxide, and benzoyl-p-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their methyl-alcoholic solutions are exposed to a mercury lamp. The yields of the isomerides are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can eventually be isolated.

[69] Ber. 1918, *51*, 214.
[67] DeFazi, Gazetta 1924, *54*, 1000.
[68] Gazz. chim. ital. 1924, *54*, 85; Atti. accad. Lincei (V), *32, ii, 227*; Chem. Abs. 1924, *18*, 2173.

Methyl anthraquinone and its mono-, chlor-, brom- and nitro derivatives have been observed by Schaarschmidt and Kasai [70] to change from a yellowish-white to a brown color on exposure to radiation from a Jaenicke mercury vapor lamp at a distance of 30 cm. Methyl anthraquinones may be arranged in the following order of decreasing sensitiveness towards this radiation: 4-chloro-1-methylanthraquinone, 2-methylanthraquinone, 3-bromo-2-methylanthraquinone, 1-nitro-2-methylanthraquinone, 1-methylanthraquinone, 3-chloro-2-methylanthraquinone, 1-chloro-2-methylanthraquinone, 1-chloro-2-dibromomethylanthraquinone, 1 : 3-dimethylanthraquinone. 1 : 3-Dimethylbenzophenone is not appreciably altered by exposure to light. Since 4-chloro-1-methylanthraquinone becomes similarly altered when rayed in an atmosphere of nitrogen or in a high vacuum, the change is considered to consist in a transformation into a colored quinonoid modification which is not completely converted into the original form when rapidly crystallized from alcohol.

Experiments on the sugars, both monosaccharides and polysaccharides, by many investigators have established the fact that they decompose more or less readily under the influence of ultraviolet of certain wave-lengths.

According to Berthelot and Gaudechon [71] simple sugars may be divided into four classes according to their resistance to light; ketoses are attacked by ultraviolet rays $\lambda = 300$ μμ (3000 Å), the aldoses by the rays $\lambda = 300$ to 250 μμ (3000-2500 Å), the straight chain polyhydric alcohols by rays $\lambda = 250$ to 200 μμ (2500-2000 Å), the ring polyhydric alcohols only by the ultraviolet of wave-length 200 μμ (2000 Å). With the longer radiations producing the first stage in the action, the liquid remains neutral and does not reduce Fehling's solution in the cold. With decreasing wave-length decomposition increases, the liquid becomes acid, and carbon dioxide can be detected in the gaseous products, the amount of hydrogen evolved increases and the solution begins to reduce Fehling's solution in the cold, and finally, methane is liberated. The volumes of carbon monoxide and hydrogen evolved in the first stage always bear a simple ratio to one another. In the case of the ketoses the solid sugars as well as their aqueous solutions undergo decomposition. Unlike the ketoses, the aldoses, dextrose, galactose and mannose are practically unaffected on exposure in aqueous solutions to sunlight.[72] They are, however, decomposed under the influence of ultraviolet rays $\lambda = 300$ to 250 μμ (3000 to 2500 Å). Carbon monoxide and hydrogen are evolved, and the corresponding alcohol, with one carbon atom less than the sugar used, is formed. Like the ketoses, secondary reactions occur when they are exposed to the extreme ultraviolet rays, carbon dioxide and methane being evolved. The liquid becomes acid and capable of reducing Fehling's solution and ammoniacal silver nitrate.

[70] Ber. 1924, *57B*, 1671.
[71] Compt. rend. 1912, *155*, 1153.
[72] Compt. rend. 1912, *155*, 831.

Euler and Ohlsen [73] exposed neutral solutions of sucrose to the rays from a Heræus quartz mercury vapor lamp and determined at intervals the rotary power, amount of invert sugar and acidity of the solutions. The experiments showed that under these conditions the sucrose is hydrolyzed and the solution becomes slightly acid. A control experiment showed that the speed of hydrolysis due to the temperature (79° C.) to which the solutions were heated by the lamp is very slow compared with that due to the action of the ultraviolet rays. The quantity of sucrose hydrolyzed is nearly as great in a 10 per cent solution as in one of double this concentration. The rate of hydrolysis increases with the duration of the exposure, this being accounted for by the acid formed in the reaction. The formation of this acid depends on a catalyst which is present in traces.

Bierry, Henri and Ranc [74] have investigated the action of ultraviolet rays from a quartz mercury vapor lamp on 5 per cent solutions of sucrose at 40° C. in vacuo and 20° C. in presence of air, with and without the addition of calcium carbonate. It is found that under the influence of the ultraviolet the sucrose is hydrolyzed to an extent which is quite appreciable after 20 hours' exposure at 40° C. while if the solution is exposed for 48 hours at this temperature it is found to contain formaldehyde. In absence of calcium carbonate gas is liberated, but this is a secondary phenomenon. The gas is scarcely perceptible before 72 hours and becomes marked on the fifth or sixth day of exposure at 40° C. Of the combustible part of this gas 50 per cent consists of carbon monoxide.[75]

Summarizing the work of earlier investigators we note that sugar in water exposed to ultraviolet is at first inverted and, as the exposure is continued, the glucose-fructose mixture is decomposed into simple aldehydes, ketones and alcohols and finally into gases (carbon dioxide, carbon monoxide and hydrogen). If glucose and fructose are radiated separately they give qualitatively but not quantitatively the same products. The higher the temperature and the shorter the wave-lengths, the more energetic is the photochemical reaction.

The photochemical decomposition of solutions of sucrose in water, has also been investigated by Beyersdorfer and Hess.[76, 77] Their experi-

[73] J. Chim. Phys. 1911, *9*, 416.

[74] Compt. rend. 1911, *152*, 1629.

[75] A résumé of the published work on the inversion of sucrose by ultraviolet rays and a reply to Bierry, Henri and Ranc is published by Berthelot and Gaudechon, Compt. rend. 1913, *156*, 468. Ultraviolet rays, Compt. rend. 1912, *155*, 1016, of relatively long wave-length photolyze di-saccharides in two stages. In the first stage hydrolysis takes place without any evolution of gas, the second stage is characterized by a regular evolution of gas due to decomposition of the mixture of monoses produced in the first stage. The solutions are reported to remain neutral throughout exposure, so that the photolysis of sucrose to dextrose and levulose and of maltose to two molecules of dextrose apparently is not brought about by the formation of acid in the solutions, as has been suggested.

[76] Ber. 1924, *57 B*, 1708.

[77] These investigators irradiated ⅛, ½ and 2 M sucrose solutions at 20°, 70° and 100° continuously 1 to 40 hours in apparatus of the Heræus type. The solutions were prepared from the purest (invert sugar-free) cane sugar

ments were carried out at temperatures of 20° C., 70° C., and 100° C. the course of the change being followed by observations of the optical rotation, acidity, and reducing power of the solutions. Reaction is scarcely appreciable at 20°, but the rate increases first slowly and then rapidly with increasing temperature. The photochemical degradation of sucrose is almost completely inhibited by the presence of chlorophyll or, to a less extent, of green-PLX.[77a] Manganese chloride, potassium chloride, potassium bromide, and potassium iodide have little influence on the change, which, however, scarcely occurs in the presence of sodium acetate. This result is not surprising, since the latter salt is known to prevent inversion of sucrose. The sucrose molecule is so stable towards the action of rays of short wave-length that the union of its component parts by an oxygen atom appears improbable. On the other hand, levulose is considerably more rapidly decomposed than dextrose. The products of the decomposition of sucrose are carbon monoxide, carbon dioxide, hydrogen, methane, organic acids, aldehydes, ketones, and alcohols, together with condensation products of the type of dextrin and caramel. A crystal of sucrose when exposed to ultraviolet rays at 70° C. becomes coated on the exposed surface with a brown layer of caramel. The prolonged exposure of sucrose solutions (99.97 per cent polarimetrically) and conductivity water and after radiation their polarization, invert polarization, acidity and reducing power were measured. At 15-20° in ⅛ M solution the effect of radiation is hardly perceptible. At 70° and 100° the sugar is attacked energetically, the decomposition at first increasing slowly, then rapidly, with increasing temperature. At 70° the d-rotation decreases and the reaction is exactly the same. Fructose alone is decomposed considerably more rapidly than glucose (7.3 and 2 times more in 4, 24 and 40 hours respectively in ⅛ M solution at 100°). If 0.3-0.6 grams chlorophyll is added to 250 c.c. of an ⅛ M solution, 12 hours radiation at 100° produces no detectable change in the sucrose. Manganese chloride (0.25-1.0 gram), potassium chloride (0.3-0.5 gram), potassium bromide (0.4 gram) and potassium iodide (0.65 gram) do not appreciably affect ⅛ M solutions radiated 4 hours. Sodium acetate (0.32 gram) so hinders the reaction that a photochemical effect can just be detected (acidity, 1 milli-normal; invert sugar, 0.35 per cent). In 0.5 M solution at 100°, gas evolution begins in 15 minutes, reaches its maximum proportionately with the time for 32 hours, while the acidity and reducing power increase approximately proportionately with the time. At 100° the same is true for the acidity during the whole exposure (40 hours). After about 4 hours, the solution becomes l-rotatory and after 24 hours contains no further positively detectable amounts of optically active substances. The reducing power reaches its maximum after about 48 hours, then decreases proportionately with the time and more slowly than it had increased. In 0.5 and 2 M solutions the course of maximum in about 4 hours and ceases in 70 hours. The composition of the gases evolved during the first 4 hours (100 c.c. from 153 c.c. solution) is carbon dioxide 5.25, oxygen 1.2, carbon monoxide 72.5, hydrogen 3.6, methane 1.2, residual gas (nitrogen) 15.9. After 16 hours they have practically the same composition. The oxygen and nitrogen come from the air in the apparatus. Replacing the air with nitrogen does not appreciably affect the results. In 1 M solution radiated 24 hours were detected, organic acids, aldehydes, ketones and alcohols. When these were removed by vacuum distillation and the residue (75 per cent dry matter) was diluted to 15 per cent with water, fermented 12 days with yeast and filtered through kieselguhr the addition of a large qualtity of alcohol precipitated from the filtrate a black-brown sticky mixture of caramel- and dextrin-like compounds, extraction with hot methyl alcohol leaving undissolved 0.6 gram (per 1. of the radiated solution) of the dextrin-like substance.

[77a] Badische Co.

to ultraviolet rays appears to yield sensibly the same products as are obtained by the dry distillation of sugar.

Neuberg [78] compares the chemical changes produced by ultraviolet rays (quartz lamp) and sunlight. Catalysts, especially iron salts, bring about marked changes in various substances exposed to sunlight. Dextrose, sucrose, lactic acid and benzoic acid were examined. Uranium salts also were employed as catalysts.

Lowry and Courtman [79] found that ultraviolet does not accelerate the isomeric change of dextrose, galactose, or maltose, of nitro-camphor, or of hydroxymethylene-camphor. In the case of aminomethylene-camphor there is a marked acceleration, which ceases when the stimulus is removed. Benzoylcamphor also undergoes isomeric change, more rapidly in presence of radiation, but the acceleration persists after the rays have been withdrawn. The permanent stimulus is probably due to the liberation of benzoic acid, which acts as a powerful catalyst in promoting isomeric change.

Experiments by Euler and Lindberg [80] show that an acid is formed from dextrose by the action of ultraviolet. On further action of the rays the acid evolves a gaseous mixture containing 15 per cent carbon dioxide, 40 per cent carbon monoxide and 40 per cent hydrogen. This gas is formed from the primary products of the action of the rays on dextrose. Incidentally it may be noted that the scission of lactic acid in pure aqueous solution into alcohol and carbon dioxide which takes place on raying is a special case of the evolution of carbon dioxide from vegetable acids. (See page 166.) Likewise the condensation of acetaldehyde, a process so important in the formation of plant acids, is a light reaction. The rate of change of lactic acid into alcohol and carbon dioxide is, within certain limits, independent of the concentration.

The results of experiments with 10 per cent aqueous solutions of different sugars, exposed for 10 hours at a distance of two centimeters from a 110-volt mercury vapor lamp according to Berthelot and Gaudechon [81] are as follows, so far as the gaseous reaction products are concerned: (1) dextrose gives approximately equal volumes of carbon monoxide and methane and about six times as much hydrogen; (2) levulose gives about ten times as much carbon monoxide as of methane; (3) maltose gives results similar to dextrose; (4) sucrose gives results intermediate between those given by dextrose and levulose. The numerical results, calculated to a basis of 100 volumes of *combustible* gas, are tabulated below:

	Carbon Monoxide	Methane	Hydrogen	Carbon Dioxide
Levulose	83	8	9	15
Dextrose	12	12	76	22
Maltose	12	11	77	21
Sucrose	45	8	47	16

[78] Biochem. Zeitsch. 1912, *39*, 158.
[79] J. Chem. Soc. 1913, *103*, 1214.
[80] Biochem. Zeitsch. 1912, *39*, 410; J. Chem. Soc. 1912, *102*, *ii*, 407.
[81] Compt. rend. 1910, *151*, 395; J. Chem. Soc. 1910, *98*, 813.

Under the influence of radiation from a quartz mercury lamp, levulose, according to Bierry, Henri and Ranc,[82] undergoes profound decomposition when in aqueous solution, carbon monoxide, carbon dioxide, formaldehyde and methyl alcohol having been recognized among the products. The reaction proceeds more readily in a vacuum than when air is present. Aldoses do not appear to undergo this degradation. Glycerol and mannitol after exposure to the rays acquire reducing properties. Berthelot and Gaudechon[83] use a 10 per cent aqueous solution of levulose to give a direct measure of the intensity of ultraviolet radiation, the volume of the gas evolved being directly proportional to the time for any given radiation, and inversely proportional to the distance. Further, for dilute solutions (4.5 to 18 grams per liter) the velocity of the reaction is proportional to the concentration, while for strong solutions (720 to 1080 grams per liter) it is constant and independent of the concentration. These facts are best explained on the hypothesis that the velocity of reaction is proportional to the quantity of rays absorbed per unit of time. A study of the action of ultraviolet on the bioses, maltose, lactrose, trehalose and gentiobiose, and the trioses, raffinose, melesitose and gentianose[84] indicates that in the case of the trioses the first stage does not consist of the formation of a monose and a biose. After the first stage of decomposition the action was the same as in the case of the monoses.

Organic compounds[85] containing a carbonyl group show exceptional sensitiveness toward light. Solutions of ketoses, protected from the air, were found to be slowly decomposed by sunlight. One c.c. of a 10 per cent solution of dihydroxyacetone evolved 0.2 c.c. of almost pure carbon monoxide on exposure to sunlight for 12 hours. Erythrulose, levulose, sorbose and perseulose were decomposed much more slowly, for with increase in the length of the carbon chain the photo-sensitiveness diminishes. A solution of levulose produced only 0.54 c.c. of gas per c.c. in about two months' time. In all cases the gas evolved was almost pure carbon monoxide. The reaction which takes place under these conditions consists in the elimination of the carbonyl group and the conversion of the ketose into an alcohol containing one carbon atom less in the molecule.[86] A similar reaction occurs under the influence of ultraviolet rays from a quartz mercury lamp, but it then proceeds much more rapidly and is accompanied by subsidiary reactions with the result that carbon monoxide produced contains some carbon dioxide, hydrogen and methane. Ketoses in the solid state are decomposed by ultraviolet rays in the same way as when dissolved in water. Bierry and Ranc[87] assert that the decomposition of levulose is much more complete than is indicated by Berthelot, carbon monoxide, carbon dioxide and formaldehyde resulting.

[82] Compt. rend. 1910, *151*, 316; see also Biochem. Z. 1914, *64*, 257.
[83] Compt. rend. 1013, *156*, 707.
[84] Berthelot and Gaudechon, Compt. rend. 1912, *155*, 1506.
[85] Compt. rend 1912, *155*, 401.
[86] See also Bull. Soc. Chim. 1924, *35*, 241.
[87] Bull. Soc. Chim. 1924, *35*, 771.

Massol [88] states that if solutions of soluble starch (prepared by heating for 3 hours at 150° C.) of 0.2 to 1 per cent concentration, are exposed, at a distance of 10 centimeters, to the action of a mercury vapor quartz lamp consuming 300 watts, the starch gradually loses the property of giving a blue color with iodine, the color undergoing an alteration similar to that observed when the iodine test is applied at various stages of starch conversion. The rate of transformation increases on decreasing the concentration and on acidifying the medium. As a result of the exposure also, the solution acquires reducing power and becomes less precipitable by alcohol. The portion soluble in alcohol possesses reducing power and is dextro-rotatory. Examination of the product obtained on exposing a solution containing 1.7 grams of soluble starch and 1.715 grams of sulfuric acid per 1000 cubic centimeters to ultraviolet rays showed that the reducing substance formed is probably maltose. A control experiment in which the solution, instead of being exposed to ultraviolet rays, was heated to 72° C. showed that neither the acidity nor the temperature conditions are capable, under the conditions of Massol's experiment, of effecting the transformation and the latter is therefore due to photochemical action. He finds that [89] soluble starch becomes hydrolyzed when its aqueous solution is exposed to a quartz mercury lamp. Changes in the rotatory power of the solution show that the transformation is probably into dextrins and maltose, although the amount of sugar isolated was insufficient for identification. The hydrolysis is not due to the small amount of hydrogen peroxide formed under the action of the rays. According to Bielecki and Wurmser [90] pure starch in aqueous solution when exposed to the ultraviolet rays undergoes hydrolysis and partial oxidation; dextrine, reducing sugars, pentoses, formaldehyde and other similar substances being formed.

It has been claimed by Witz that the action of light on cellulose produces oxycellulose, while Girard has asserted that the product is more probably hydrocellulose. To furnish further data on this moot point Dorée and Dyer [91] exposed some specially scoured and bleached cotton cloth to the rays of the Cooper-Hewitt mercury vapor lamp continuously for a period of one week and then tested the exposed cloth in various ways. The conclusion is drawn that ultraviolet rays under the conditions employed, convert cellulose with complete loss of tensile strength into oxycellulose.

[88] Compt. rend. 1911, *152*, 902.
[89] *Loc cit.*
[90] Compt. rend. 1912, *154*, 1429.
[91] J. Soc. Dyers Colorists 1917, *33*, 17; Chem. Abs. 1917, *11*, 1753.

Chapter 9.

Photochemical and Photolytic Reactions (Continued)

The action of ultraviolet light on many organic acids or their salts leads to decomposition, but in the cases in which there is unsaturation, the polymerization and isomerization characteristic of multiple bonds often results.

The influence of light upon various acids and their salts is interpreted by Jaeger and Berger [1] largely by ionic equations, and from the results it is concluded that each photochemical reaction is specific and very dependent upon conditions obtaining at the moment, so that it is scarcely ever possible to predict its course. Among the conditions governing the reaction the presence of certain ions in the solution must be considered a factor of great importance. In the photochemical decomposition of salts the velocity of reaction is greatly influenced by the presence of certain cations in the solution. The addition of certain neutral salts first increases the velocity and on further addition retards it or completely stops it. The greater the electrical charge of the cation of the salt added, the smaller the quantity required to bring the rate of decomposition to a maximum.[2]

Kailan [3] has found that when dilute (0.5 to 2 N) solutions of acetic, oxalic, malonic, succinic, malic and tartaric acid are exposed in quartz cells to the action of a quartz mercury lamp, slight decomposition takes place. The speed of decomposition of a dibasic acid is increased by the introduction of an alcoholic hydroxyl group into the molecules. No decomposition takes place under similar conditions in glass vessels. The speed of decomposition increases with length of exposure, but does not increase in proportion to increasing concentration of the acid. Any dissolved oxygen plays only a subordinate part, since the acid solution shows at most only a slight reduction in the speed of decomposition when all air has been expelled.

Volmar [4] also states that under the influence of ultraviolet rays,

[1] J. Chem. Soc. 1921, *119*, 2070.

[2] Proc. Roy. Soc. 1920, *23*, 84. In Rec. Trav. Chim. 1922, *41*, 71, is reported the result of the exposure of aqueous solutions of organic acids and salts, most of which contained the halogen radical. These compounds are split up in various ways, giving formaldehyde, carbon dioxide, hydrogen, chlorine, etc., depending on the substance and the exposure.

[3] Monatsh. Chem. 1913, *34*, 1209.

[4] Compt. rend. 1923, *176*, 742; J. Chem. Soc. 1923, *124*, *ii*, 279; J. S. C. I. 1923, *42*, 423 A.

and to a much lesser degree in sunlight, hydroxy-acids and their salts undergo photolysis. Tartaric acid in 1 per cent solution after three hours' exposure gave 3.5 c.c. of gas having the composition CO_2 66 per cent, CO 10 per cent, H_2 21 per cent, hydrocarbon 3 per cent. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In presence of alkalies, the carbon monoxide may disappear entirely, owing to condensation with a portion of the hydrogen, forming the above-mentioned aldehydic substances. The homologues of tartaric acid behaved in a similar way. The decomposition is accelerated by the presence of catalysts such as uranyl acetate.

The formation of reducing substances and carbon dioxide, when tartaric acid is exposed to ultraviolet rays, is noted by Euler and Ryd.[5] In this case, ferric (not ferrous) salts increase the rate of gas evolution, being reduced themselves at the same time.

Volmar[6] finds that solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper and iron undergo decomposition on exposure to ultraviolet radiation with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. The simple salts of the same metals, both organic and inorganic, are quite stable under similar conditions. The conclusion is drawn that the heavy metal in the tartrates occupies a position in the molecule in accordance with the constitution attributed to it by Jungfleisch. Potassium borotartrate furnishes an exception; Volmar considers this to be due to the fact that it appears to be, not a definite compound, but a mixture.

It has been found by Baudisch[7] that when lactic acid, which has been repeatedly purified from its zinc salt, is put in Heræus quartz flasks and exposed to the rays of Heræus quartz mercury lamp (250 v. and 3 to 5 amp.) for about forty hours the distillate after neutralization with calcium carbonate gives decisive acetic acid reactions. Further experiments failed to show that either alcohol or methane are products of the action of raying lactic acid. When irradiated with ultraviolet, solid calcium lactate gives carbon monoxide, methane, ethane and hydrogen.[8] The proportion between this and the carbon dioxide is about the same as when these gases are produced in the butyric fermentation.

According to Euler[9] the degradation of lactic acid to carbon dioxide and alcohol takes place in pure aqueous solution under the influence of ultraviolet radiations. The rate of decomposition of the lactic acid does not depend on the concentration of the acid within the limits studied. The decomposition of lactic acid in ultraviolet has been investigated by Euler and Ryd.[10] Lactic acid in the presence of the short ultraviolet rays undergoes a decomposition, analogous to

[5] Biochem. Zeitsch. 1913, *51*, 97.
[6] Compt. rend. 1923, *176*, 1465; J. Chem. Soc. 1923, *124*, *ii*, 453.
[7] Biochem Z. 1920, *103*, 59; Chem. Abs. 1920, *14*, 2776.
[8] Berthelot and Gaudechon, Compt. rend. 1910, *151*, 478.
[9] Arkiv. Kem. Min. Geol. 1911, *4*, No. 8, 1; J. Chem. Soc. 1912, *102*, *ii*, 112.
[10] Biochem. Zeitsch. 1913, *51*, 97; J. Chem. Soc. 1913, *104*, *ii*, 544.

a fermentation, with evolution of carbon dioxide. This reaction is less influenced by temperature than other photochemical reactions. The rate of evolution of carbon dioxide is not accelerated by the presence of either ferrous or ferric salts, but the latter are reduced.

According to Holmes and Patrick [11] silica gels impregnated with acetic acid or acetone on exposure to ultraviolet rays give off gaseous products which consist of a mixture of the organic liquid and its photochemical decomposition products. An experimental investigation of the hydrolysis of monochloroacetic and monobromoacetic acids under the influence of ultraviolet has been made by Rudberg (Z. Physik. 1924, *24*, 247). The number of chlorine or bromine atoms freed by the action of monochromatic light was determined electrometrically. A concentration of chlorine or bromine ions corresponding with a silver deposit of 0.001 mg. could be estimated. The radiant energy absorbed was determined by a sensitive thermopile. In the case of both acids, the action of the rays became noticeable between 313 and 266 μμ (3130 and 2660 Å) and the measurements were carried out for $\lambda = 253.6$ μμ (2536 Å). In the case of chloroacetic acid the action follows the Einstein law, $N = Q/h\nu$. For monobromoacetic acid, the number of molecules transformed is only 0.34 of the number of quanta absorbed. This fraction increases as the solution changes from acid to alkaline, but the increase is shown to be inconsistent with the assumption of a simple collision reaction between the active molecules and hydroxyl ions.[12]

The photochemical reactions between bromoacetic acid and alcohol and between chloroacetic acid and alcohol have been studied by Cassel.[13] The reactions were carried out in a transparent quartz vessel which was irradiated by an arc lamp of 1800 candle power. It has been found that decomposition into methyl alcohol, acetic aldehyde and the halogen acid occurs. The reaction is only sensitive to ultraviolet rays of a wave-length of less than 250 μμ (2500 Å). It has been observed that the bromine compound is more easily decomposed by alcohol, both in the light and in the dark, than the chlorine compound. In aqueous solution the halogen has been found to split off from 1-bromosuccinic acid more readily in the light than 1-chlorosuccinic acid in a corresponding solution. Euler [14] has stated that when haloacetic acids in dilute water solution are exposed to the ultraviolet rays of a mercury lamp, halogen is split off at 18° with a velocity corresponding to that attained when the non-irradiated solutions are heated to about 100°. The reaction differs from that in the dark in being of a lower order, increasingly smaller amounts of the halogen compounds decomposing per unit of time as the concentration increases. The reaction seemed to Euler to be well adapted to answering a question of importance from

[11] J. Phys. Chem. 1922, *26*, 25.

[12] The exposure of an alcoholic solution of 5-tetralylen acetic acid to the radiation of a quartz mercury lamp yields dihydronaphthyl acetic acid. Schroeter, Ber. 1925, *58*, 713.

[13] Z. physik. Chem. 1916, *92*, 113.

[14] Ber. 1916, *49*, 1366.

the photochemical standpoint, namely, whether irradiation before the photochemical decomposition produces a loosening of the atomic unions in the molecule; specifically, whether a considerable part of the light-sensitive chloroacetic acid possesses after the illumination an atomic grouping still corresponding to the usual formula for the acid but characterized by greater liability of reactivity in reaction in the dark.

In flat quartz vessels 0.5 N solutions of dry chloroacetic acid in benzene kept at 27° (under these conditions no measurable amount of chlorine is split off without irradiation in the time intervals used) were exposed at a distance of 7 centimeters to the light of a Heræus quartz mercury lamp. After 150 minutes 5 cubic centimeters of the solution were shaken with 10 cubic centimeters of 0.5 N caustic soda, heated 30 minutes at 70°, quickly cooled, freed from benzene, acidified with nitric acid, treated with silver nitrate at room temperature and the silver chloride determined in the usual way after standing a long time. A parallel determination with a solution kept in the dark was made simultaneously. The irradiated solutions gave 0.0328 gram silver chloride, the control, 0.0272 gram. That the excess in the first case (0.0022 gram per hour irradiation) was split off during the raying, although the solvent was benzene was shown by precipitating the silver chloride immediately after shaking the solution with caustic soda. The rayed solution gave the same amount of silver chloride (0.0024 gram) per hour, the control test, none. This, in conjunction with the preceding experiments, also shows that the part of chloroacetic acid undecomposed by irradiation is decomposed by caustic soda with the same velocity as the control. To determine the nature of the decomposition produced by the radiation, large amounts of the rayed solutions in benzene were shaken out with alkali, acidified with sulfuric acid, freed from most of the chloroacetic acid by steam distillation, extracted with ether, dried, evaporated and treated with chloroform to remove the rest of the chloroacetic acid; the residue heated to 200-250° gave a sublimate of fumaric acid. The presence of an unsaturated acid was also detected by the behavior of the alkaline extract of the reaction solution towards dilute potassium permanganate, 3.5 cubic centimeters of a 0.01 N solution of which was decolorized by 5 cubic centimeters of a 0.5 N solution chloroacetic acid in benzene, rayed four hours. If the rayed solution is shaken, with water, instead of caustic soda, until nearly all the acid is removed, then treated with chloroform and again shaken with water, the dried benzene-chloroform extract yields glycolide melting at 82°. Shaking the benzene with alkali also yields a small amount of polyglycolide. From the solubility relations of fumaric acid it appears that another unsaturated acid more soluble in benzene, ether and chloroform is also formed. In ether instead of benzene the results are qualitatively the same but more chlorine splits off (corresponding to 0.006 grams silver chloride per hour irradiation). In water solution the difference between the decomposition velocity of the undissociated acid and the chloroacetic acid is smaller under radiation than the non-radiant. In benzene, bromacetic acid is decomposed more quickly than chloroacetic acid; contrary to what occurs in water solution when rayed, but in agreement with the results obtained without such exposure.[14a]

Acetic acid and aniline [15] in equimolecular proportions when exposed to ultraviolet rays for 24 hours give nearly a 100 per cent yield of acetanilide. Propionic and benzoic acids act similarly, but the yield of propionanilide is only about 65 per cent, and that of benzanilide considerably less. Amide formation occurs much less readily, ammonium acetate in the presence of excess ammonium hydroxide giving only about 5.3 per cent acetamide, and ammonium benzoate even less benzamide.

[14a] Chem. Abs. 1917, *11*, 942.
[15] Stoermer and Robert, Ber. 1922, *55 B*, 1030.

Hanssen [16] asserts that many photochemical actions such as the decomposition of oxalic acid and hydrochloric acid and the union of carbon monoxide and chlorine, are subject to the ordinary law of mass action. Experiments relating to the photochemical decomposition of oxalic acid indicate that this reaction is unimolecular, and from the total change in the electrical conductivity Boll [17] draws the conclusion that the chemical reaction corresponds with the equation $H_2C_2O_4 + O = 2CO_2 + H_2O$. Uranyl nitrate in the solution acts as a catalyst. In agreement with the observed unimolecular character of the reaction, it is found that the velocity is proportional to the quantity of light absorbed by the solution, and that this proportionality is independent of the concentration of the oxalic acid. The decomposition of oxalic acid by uranium and its compounds has been investigated by Landau [18] and shown not to be parallel with the radio-activity of the substances used. The lightest and heaviest metal of each of six groups of the periodic table were also tried in the form of nitrates, and of these only chromium and uranium (group VI) proved to be active, uranium being three times as active as chromium. Various solutions of 0.1 N strength were exposed at 25° in a quartz flask to a Cooper-Hewitt quartz mercury vapor lamp at 10 centimeters distance by Mathews and Dewey.[19] Under these conditions oxalic acid is very slightly affected but in the presence of uranuim nitrate, sulfate or acetate is rapidly oxidized at a linear rate proportional to the uranium concentration. It is deduced that the decomposing action of ultraviolet is dependent on the amount of radiation photochemically absorbed. The photolysis of oxalic acid [20] consists in the primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the nascent acid into carbon monoxide and water by rays of long wave-length and into carbon dioxide and hydrogen by waves of short length. This further shows that the radiant energy represents a lower form than thermal energy and that the frequency of vibration plays the same rôle in the former as does the temperature in the latter. Holmes [21] notes that the photochemical decomposition of oxalic acid in the presence of uranium salts is quantitative and might be employed in connection with the determination of the light fastness of dyes.

According to Büchi [22] the photolysis of oxalic acid in presence of uranyl salts is to be attributed to the decomposition of the non-ionized molecules of uranyl oxalate ($UO_2C_2O_4$), or of the complex ions ($UO_2(C_2O_4)_2$). When oxalic acid is present in excess of the equimolar ratio, the velocity of decomposition is independent of the concentration of the oxalic acid, and is approximately constant. If the proportion of oxalic acid is smaller, the sensitiveness to light is, however,

[16] Compt. rend. 1907, *145*, 564.
[17] J. Chem. Soc. 1915, *108, ii*, 123.
[18] Compt. rend. 1913, *156*, 1894.
[19] J. Physikal. Chem. 1913, *17*, 211.
[20] Compt. rend. *158*, 1791.
[21] Amer. Dyestuff Rep. 1924, *13*, 188, 197.
[22] Z. physikal. Chem. 1924, *111*, 269.

approximately proportional to the concentration of the oxalic acid. The great stability of the complex is indicated (a) by the quantitative equality of the velocity of decomposition for systems of uranyl sulfate, nitrate, and oxalate in presence of oxalic acid, (b) by the permanence of the complex on the addition of oxygen, hydrochloric acid, sulfuric acid, and formic acid. The photolytic decomposition follows Einstein's law, one absorbed light quantum decomposing 1 mol. of oxalic acid. In the initial stages of the decomposition of uranyl formate in sulfuric acid solution one absorbed light quantum decomposes about 0.7 mol. of formic acid. In 1917 Bauer [23] suggested that the photolysis of oxalic acid corresponds with the equation $H_2C_2O_4 + 1h\nu = H_2O + CO + CO_2$, but subsequently [24] expressed the view that the reaction is diquantic, glyoxylic acid being formed as an intermediate product. In view of the results of Büchi, Bauer now concludes that the oxalic acid ion is directly decomposed into carbon monoxide and carbon dioxide with the absorption of one light quantum. It is also probable that formate photolysis likewise requires one quantum.

Kunz-Krause and Manicke [25] report that under the catalytic action of ferric chloride 5.3 per cent of crystalline oxalic acid suffers decomposition with evolution of carbon dioxide after a 5 hour arc light exposure; 61.7 per cent after 16 hours. With ammonium oxalate and in the presence of mercuric chloride, 12.46 per cent decomposes after 2 hours. Uranyl acetate and iodic acid effect decomposition of crystalline oxalic acid to the extent of 5.49 and 4.55 per cent respectively, after a 4- and a 3-hour exposure. Chromium chloride cannot replace ferric chloride as catalyzer in such experiments on oxalic acid. Berthelot and Gaudechon [26] studied the photochemical decomposition of anhydrous oxalic acid and reported that it was decomposed by ultraviolet of wave-length shorter than 300 μμ (3000 Å). Analysis of their products showed 87 per cent of carbon dioxide, 9.5 per cent of carbon monoxide and 3.5 per cent of hydrogen together with traces of formic acid. The temperature of the acid attained 95°, probably due to the proximity of the mercury arc lamp, which was placed at a distance of only 2 cm. Investigations of the effect of ultraviolet of wave-length from the visible spectrum to 250, 220, 185 and 100 μμ (2500, 2200, 1850, and 1000 Å) on the decomposition of oxalic acid solutions and the solid acid have been made by Noyes and Kouperman.[27] They found that anhydrous oxalic acid is decomposed by rays of wave-length shorter than 250 μμ (2500 Å). The rate is greater for short wave-lengths, is much increased by the presence of water and evidently depends on the amount of water present. In the case of the solution a large portion of the radiant energy is undoubtedly transmitted, so that this rate is not directly comparable with the other. It is significant that despite this fact the rate is greater than for the anhydrous solid. Since

[23] Z. physikal Chem. 1924, *111*, 315.
[24] Cf. J. Chem. Soc. 1919, *116*, *ii*, 264.
[25] Ber. pharm. ges. 1922, *32*, 209.
[26] Compt. rend. 1914, *158*, 1791.
[27] J. Am. Chem. Soc. 1923, *45*, 1398.

water vapor may be one of the products of the decomposition, the reaction is autocatalytic. There is a long induction period which may be explained in this manner or in either of two other ways. (1) It may be due to the slow formation of formic acid, the latter being rapidly decomposed. In this case the rate of reaction would not reach a maximum until the rate of formation of the formic acid had become constant. This explanation seems hardly acceptable, although formic acid is evidently rapidly decomposed by the radiation from the mercury arc lamp. (2) It may be due to slow rate of diffusion out of the solid and away from the surface. This factor would not be important if only the surface molecules were decomposed. If molecules in the interior of the crystals were decomposed the gases formed would only slowly diffuse out and the rate of reaction as measured by the pressure would become constant only when a mobile equilibrium was established, the number of molecules of gas diffusing out being then equal to the number formed by the action of the radiation. The effect of higher frequencies in causing more rapid decomposition may be partially explained in this way, since the energy, beyond that actually necessary to decompose the molecules, might be converted into kinetic energy causing the products of the decomposition to diffuse out more rapidly. After the induction period the rate of decomposition is practically constant.

The decomposition of a solution of potassium cobaltioxalate[28] by raying was studied by Jaeger and Berger,[29] who used a quartz mercury lamp and carried out the reaction in quartz vessels. The quantities of salt decomposed in identical intervals of time are approximately independent of the initial concentration, and are chiefly determined by the light energy absorbed. An exact relation between the amount of decomposed substance and the time of exposure, with the same initial concentration is not found, which is attributed to the change of absorptive power of the solution. When using the pure salt it is found that the speed of reaction is relatively greater on working with dilute solutions, although there appears to be some disturbing influence present. The addition of alcohol has no appreciable effect, but neutral salts such as the chlorides of potassium, sodium, lithium, magnesium, glucinium and iron (ferric) exert a strong influence on the speed of reaction.

Padoa and Minganti[30] have measured the temperature coefficients of Eder's reaction, $2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2$, proceeding under the influence of lights of various wave-lengths. Besides white light, ultraviolet rays, with the luminous zone $\lambda = 400$ to 280 μμ (4000 to 2800 Å), and maximum intensity of 366 μμ

[28] An investigation by Schwarz and Weiss, Ber. 1925, *58*, 746, to determine the action of ultraviolet rays on cobalt nitrito-ammin complex salts in aqueous solution showed hydrolytic decomposition to occur at a maximum in the region 366 μμ (3660 Å).

[29] Proc. K. Akad. Wetensch. Amsterdam 1920, *23*, 84; J. Chem. Soc. 1920, *118*, ii, 725. See also investigations of Berger, Rec. trav. chim. 1925, *44*, 47, on the photolysis in ultraviolet radiation of several complex cobalt salts.

[30] Atti. R. Accad. Lincei. 1915 (v), *24, ii*, 97; J. Chem. Soc. 1915, *108, ii*, 719.

(3660 Å), dark blue with the zone $\lambda = 478\text{-}410$ μμ (4780-4100 Å), and the maximum at 366 μμ (3660 Å), and the green with the zone $\lambda = 540\text{-}505$ μμ (5400-5050 Å), and the maximum at $\lambda = 533$ μμ (5330 Å) were used. In the case of the green light, the reaction proceeds so slowly that a little dilute aqueous tetrabromofluorescein was added as a sensitizer; the latter was also employed in some of the experiments with white light. For the temperature interval 20-40°, the temperature coefficients are as follows: white light 1.29; ultraviolet 1.05; dark blue 1.21; green with sensitizer 1.75; white with sensitizer 1.50. In accordance with the results previously obtained with phototropic substances, the temperature-coefficients increase with the wave-length of the activating light. With white light, the sensitizer used raises the temperature-coefficient considerably, since it gives preponderance to the action of the yellow and green rays, which without it are of slight activity. Red light has no action even in presence of a sensitizer. Certain evidence indicates that, in the assimilatory process of plants under the influence of chlorophyll, the temperature-coefficient is considerably greater than 1.

Experiments have been made by Winther [31] relating to the influence of iron and oxygen on the photochemical sensitiveness of Eder's solution. The sensitiveness is very largely dependent on the purity of the mercuric chloride and the ammonium oxalate which are used in the preparation of the solution. The active impurity is iron, and experiments with solutions containing very small quantities of ferric chloride show that the photochemical sensitiveness is proportional to the iron content. These observations lead to the conclusion that a solution of mercuric oxalate which is completely free from iron would not exhibit any photochemical effect. It was later shown that this conclusion did not agree with Eder's observations [32] leading to a further series of experiments with solutions prepared from carefully purified substances. These experiments show that the photochemical sensitiveness of solutions of mercuric oxalate (mercuric chloride and ammonium oxalate) is not dependent on the presence of traces of ferric salts, but is also exhibited by the pure mercuric compound. The decomposition of the mercuric salt is mainly determined by the ultraviolet rays, but comparative observations have shown that the relative activity of the visible rays is increased if the solution contains small quantities of iron. The precipitation of mercurous chloride from Eder's solution, on exposure to light, reaches a limit when the solution still contains large quantities of mercuric chloride and ammonium oxalate. Comparative experiments by Winther and Howe [33] in which equal volumes of the filtrate and of a fresh solution of the same composition were exposed to the influence of light under similar conditions, indicate that the initial photochemical action leads to the formation of some substance which acts as a powerful negative catalyst. The same phe-

[31] Zeitsch. wiss. Photochem. 1910, *8*, 197; J. Chem. Soc. 1910, *98*, *ii*, 564. See also Berger, Chem. Abs., *16*, 1175.
[32] Zeitsch. wiss. Photochem. 1914, *14*, 172; J. Chem. Soc. 1915, *108*, *ii*, 199.
[33] Zeitsch. wiss. Photochem. 1913, *13*, 89; J. Chem. Soc. 1914, *106*, *ii*, 10.

nomenon is met with in the case of Eder's solution to which eosin is added. In general, the effect becomes more marked as the intensity of the light increases. If the ultraviolet rays are cut off during the preliminary exposure, the photochemical sensitiveness does not disappear. Further, it has been found that there is an appreciable loss of sensitiveness if the eosin solution is insolated before adding to the Eder's solution. The observations seem to show that the anti-catalyst which reduces the photosensitiveness of the solution is a product of the photochemical decomposition of eosin.

Padoa and Vita [34] studied the action of light on two reactions: first, the oxidation of hydrogen iodide, and second the reaction,

$$2FeCl_3 + H_2C_2O_4 \longrightarrow 2FeCl_2 + 2HCl + 2CO_2.$$

For the first the sum of the effects of the blue, green and violet zones is 3.17 times the effect produced by unfiltered light. For the second reaction the spectral region over which the action takes place is somewhat limited, but the sum of the effects obtained in the blue and violet regions is 1.123 times that of white light. In the presence of quinine hydrogen sulfate the zone of active radiations is widened and the sum of the effects of blue, green, and violet lights is 2.125 times that of white light.

Winther and Howe [35] have made a study of the photochemical decomposition of iron oxalate, succinate, tartrate, citrate and acetate for short wave-lengths, chiefly ultraviolet. The reaction velocity is approximately constant throughout the whole change. The "quantum-sensitiveness" is greater than unity, showing a catalytic light reaction. In terms of unit quantity of incident light, the sensitiveness at a given concentration increases as the absorption coefficient of the solution decreases. This may be ascribed to the existence of two substances, one photosensitive, the other insensitive and causing most of the absorption. The effect of the incident light also increased with increasing dilution.

In the course of some investigations on the salts of phthalic acid, which were carried out by Ekely and Banta,[36] lead phthalate was exposed in a small quartz crucible to the action of a quartz mercury vapor lamp. The outside layer of the salt decomposed rapidly with the formation of a yellowish brown substance of unknown composition, probably containing lead oxide. A similar experiment performed with mercuric phthalate showed the salt to be unaffected.

Mixtures of fumaric and maleic acid in one-fiftieth normal solutions, containing various percentages of maleic acid have been subjected by Kailan [37] to the radiation of eighty to one hundred and ten milligrams of radium metal through one millimeter of glass for from

[34] Gazetta 1924, *54*, 147; see also Atti. Cong. maz. chim. para applicata 1923, 398.
[35] Z. Wiss. Phot. 1914, *14*, 196.
[36] J. Amer. Chem. Soc. 1917, *39*, 762.
[37] Zeitsch. physikal. Chem. 1920, *95*, 215; J. Chem. Soc. 1920, *118*, *ii*, 576.

two to three thousand hours at 6°-14° C. On the assumption that the decrease in the titre of the solution is due to the formation of acrylic acid, it is found that in all cases but one the maleic acid concentration has increased. A normal solution of urea radiated for 1632 hours with the rays from eighty milligrams of radium metal, or for 48 hours by a quartz mercury lamp, showed no change in the density, refractive index, or the velocity of change into ammonium cyanate, other than could be accounted for by the experimental error. Similar treatment of aqueous solutions of formic acid changes neither the dissociation constant nor the amount of oxalic acid formation. Both types of radiation induce a decrease in the titre of the solutions, the rate of which decreases as the concentration increases. Only rays with a smaller wave-length than 340 μμ (3400 Å) are active. A similar treatment of aqueous solutions of benzoic acid produces reducing substances, formic acid and oxalic acid, the velocity of formation of these substances increasing as the square of the concentration of the benzoic acid. The equilibrium which exists between fumaric and maleic acids and the velocity of transformation in either direction was also determined.[38] The transformation was carried out in aqueous solutions of the acids of 0.084 N and these were subjected to the action of a quartz mercury lamp in vessels of glass and of quartz. In the solid condition fumaric acid is not converted into maleic acid by ultraviolet, while maleic acid is converted into fumaric acid only to the very slightest extent. In aqueous solution whether the solution was contained in glass or in quartz vessels, an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the maleic acid side with increasing concentration. Thus at 45-50° with 1/10 N-solution the equilibrium mixture contained 75 per cent of maleic acid and in 2/5 N-solution 79 per cent of maleic acid. The velocity of transformation was much greater in quartz vessels than in glass vessels, while the position of the equilibrium is uninfluenced. Maleic acid is formed when a mixture of benzoic and formic acids is exposed either to the action of ultraviolet or to the penetrating radium rays.[39] Formic acid is decomposed by the action of radiation from a quartz mercury vapor lamp, and benzoic acid is converted into formic acid in the same manner.

In the photochemical conversion of one isomeric substance into another an obstacle seems to be that after the initial disruption of the molecule, the constituents more frequently return to the original form than to that of the isomer, and this view is taken by Warburg[40] as the reason for such small yields of conversion of fumaric into maleic acid.

Eggert[41] finds that the transformation by light of ethyl malate

[38] Kailan, Zeitsch. physikal. Chem. 1914, *87*, 333; J. Chem. Soc. 1914, *106, ii*, 449.
[39] Kailan, Monatsh. 1920. *41*, 305; Chem. Abs. 1921, *15*, 1100.
[40] Sitzb. Preuss. Akad. Math.-Phys. 1919, 960; Chem. Abs. 1920, 1931.
[41] Physik. Z. 1923, *24*, 504; Chem. Abs. 1924, *18*, 3548.

into fumaric acid is sensitized by bromine. The reaction is carried out in carbon tetrachloride solution. The transformation is proportional to the number of quanta absorbed; is independent of the bromime concentration within the limits 1:9, and independent of the carbon tetrachloride concentration within the limits 1:5. It is suggested that bromine is first activated by the absorption of light, the active bromine subsequently transforming the molecules of the malic ester into fumaric acid.

Stoermer and Robert [42] first found that the rearrangement of crotonic acid into isocrotonic acid with the help of a Schott uviol lamp was not certain but that the elements of water, methyl and ethyl alcohols can easily be added to the double bond under the influence of ultraviolet. On the other hand, the rearrangement of the amide of crotonic acid into that of isocrotonic acid was easily effected. Later, starting with pure crotonic acid and using a Heræus quartz lamp, crotonic acid also has to a small extent been rearranged into isocrotonic acid. As it is very difficult to obtain isocrotonic acid in pure crystallized form, the amount formed was determined by converting it into the amide. A further study of the addition reactions in ultraviolet showed that aniline and ammonia also add with the greatest ease at the double bond of α, β-unsaturated acids; crotonic acid and aniline give, together with a little of the anilides of crotonic and isocrotonic acid, chiefly $CH_3CH(NHC_6H_5)CH_2CO_2H$ and some of its anilide while ammonia yields chiefly $CH_3CH(NH_2)CH_2CO_2H$ and iminodibutyric acid, with only very little of the amide of crotonic acid. Autenrieth and Pretzel [43] believe that the reaction between crotonic acid and aniline, at least on heating at 180-190°, consists first in the formation of the anilide, which then adds aniline at the double bond, but Stoermer and Robert think that although in ultraviolet the reaction takes place at a very low temperature the mechanism is similar in both cases. As to the anilides of crotonic and isocrotonic acids it is not believed that they are formed during the distillation of the product, which was carried out in vacuo, nor from the aniline addition product of the anilide, which is always formed in very small amount and only in the presence of an excess of aniline. The separation of the two anilides is extraordinarily difficult and even on irradiating the pure stable anilide the amount of isoanilide obtained was not sufficient to permit of complete separation by careful fractional crystallization. With the Heræus lamp the maximum rearrangement (40%) of the amide of crotonic acid in acetone is attained in about 2 days. For the rearrangement of crotonic acid, toluene proved the best solvent. Acrylic acid similarly treated with aniline gives $C_6H_5NHCH_2CH_2CONHC_6H_5$, and the deliquescent hydrochloride, melting about 64°, of $C_6H_5NHCH_2CH_2CO_2C_2H_5$ a light yellow oil. From crotonic acid and paratoluidine was obtained ethyl β-*p*-toluidineobutyrate.

[42] Ber. 1922, *55 B*, 1030; Chem. Abs. 1922, *16*, 3631; see also Chem. Abs. 1914, *8*, 2880.
[43] Ber. 1903, *36*, 1263.

A number of esters of substituted acrylic acids have been studied by Rice. The yellow methyl and ethyl esters of benzoylacrylic acid are transformed in the sunlight into the corresponding stereo-isomeric colorless esters. The reverse transformation of the colorless into the yellow esters takes place if the former are exposed to the sunlight in solutions containing a trace of iodine or bromine.[44] In a similar manner the yellow methyl and ethyl esters of p-methoxy-benzoyl acrylic acid on exposure to the sunlight in benzene solution are transformed into the corresponding colorless isomeric esters. The reverse transformation of the colorless into the yellow esters again results when solutions of the colorless solids containing a crystal of iodine are exposed to the sunlight.[45] The yellow methyl and ethyl esters of p-ethoxy-benzoylacrylic acid isomerize when exposed to the sunlight both as solids and in benzene solution. The unstable, colorless esters thus formed are transformed quantitatively, both in the dark and in the sunlight when in benzene solutions containing a crystal of iodine, into the stable yellow isomers. Hydrochloric acid brings about the same change.[45a]

According to Reimer[46] the products formed by action of the sunlight on methyl benzalpyruvate exposed in the dry condition are a polymeric ester, melting at 154° C., obtained in small quantity, and an oil, probably a mixture of isomers and decomposition products. On exposure in benzene solution, a reaction which in other cases almost invariably gives an isomeric compound, the product of reaction was found to be a polymer, melting at 117° C. Reactions with these two polymeric substances have shown that the higher melting has the structure of the truxillic acid series, while the lower melting one is related to the truxinic acids. The formation of the latter compound may be explained on the assumption that in solution isomerization had taken place and that the isomeric ester had polymerized. The reaction is an unusual one as but few cases of polymerization of this type of substance in solution have been described.[47]

A comparison of this ester, I, with that of benzoyl-acrylic acid, II,

$$\underset{\text{I}}{C_6H_5CH=CHCOCOOCH_3} \qquad\qquad \underset{\text{II}}{C_6H_5COCH=CHCOOCH_3}$$

is of interest. The system of "conjugated double linkages" in the two is the same but stands in a different relation to the phenyl and the carboxyl groups. The products obtained from I are polymers, while on exposure of II to the sunlight no polymers are formed but isomerization takes place with the greatest ease. Whether the difference in reaction of these two substances is due to difference in the chemical effect of the neighboring groups on the unsaturated part of the molecule or to a difference in the physical state of the compounds during exposure is still to be determined.

When specimens of cinnamic acid, melting point 42°, obtained from the acids, melting points 68° and 58°, are exposed to bright daylight during two years, the resulting product consisted of unchanged acid and β-truxillic acid,[48] but when samples having the melting points 42°, 58°, and 68° were exposed in quartz tubes to direct sunlight which was sufficiently powerful to cause temporary fusion, with consequent isomerization, the product consisted chiefly of α-truxillic acid with little β-truxillic acid and small quantities of trans-cinnamic acid and benzoic acid. The light reactions of cis- and trans-cinnamic acids have been further studied by Stobbe and Steinberger.[49] They find,

[44] J. Am. Chem. Soc. 1923, *45*, 222.
[45] Ibid. 1924, *46*, 214.
[45a] Ibid., p. 2319.
[46] J. Am. Chem. Soc. 1924, *46*, 783.
[47] See Ciamician and Silber, Ber. 1909, *42*, 1388; Stobbe and Rücker, Ber. 1911, *44*, 869; Reimer and Kelly, Am. Chem. J. 1913, *50*, 157.
[48] Stobbe, Ber. 1919, *52 B*, 666.
[49] Ber. 1922, *55 B*, 2225; Chem. Abs. 1923, *17*, 549.

as did de Jong,[50] that exposure of cis-cinnamic acid to sunlight gives besides the expected β-truxinic acid, trans-cinnamic acid and α-truxillic acid. Exposure for 96 hours of the liquid melt of cis-cinnamic acid to the rays of a quartz-mercury lamp produced extensive isomerization into trans-cinnamic acid, but neither β-truxinic nor α-truxillic is formed, the melt thus behaving like benzol or methyl alcohol solutions. It may be said in general that irradiation of the cinnamic acids in the liquid state (solution or melt) produces isomerization but no polymerization. The chief action is ascribed to rays from 270 to 320 μμ (2700 to 3200 Å) although the shorter and the longer rays are also not without influence.

The isomerization reaction proceeds in the same way in both the mercury arc rays and in sunlight, but the yield of dimers is very different. Taking each day of exposure as equal to seven hours, cis-cinnamic acid after 200 hours in the mercury arc ray gives 4.4 per cent dimers, and after 196 hours in the sunlight 71.0 per cent. For trans-cinnamic acid the values are 2 per cent after 364 hours in the mercury arc ray and 85.7 per cent after 161 hours in the sunlight. Long ultraviolet rays favor polymerization, while the shorter rays hinder it, and exert a depolymerizing action on the truxinic and truxillic acids. Comparison of these sunlight experiments with those of de Jong [51] and of Stoermer [52] shows that cis-cinnamic acid yields β-truxinic acid always, and generally in predominant amount, but that, especially on long illumination, there is also isomerization into trans-cinnamic acid, and subsequent polymerization to α-truxillic acid. Trans-cinnamic acid, on the other hand, is almost exclusively polymerized to α-truxillic acid; only on long illumination are there formed relatively small amounts of β-truxinic acid, accompanied by considerable resinification.

Experiments with mixtures of equal parts of cis- and trans-cinnamic acids show that the trans-cinnamic acid mixed with the cis- form produces no increase of *β*-truxinic, and that therefore, contrary to de Jong's belief, α-truxinic acid is formed only from two molecules of cis-cinnamic acid. In agreement with Stoermer and Scholtz,[53] Stobbe and Steinberger conclude that *β*-truxinic acid has a meso and not a racemic structure. Experiments by Stobbe and Lehfeldt have shown that the *β*-arylacrylic acids, including trans-cinnamic acid, are dimerized and autoxidized to benzaldehyde, both in the solid state and in aqueous suspension. Both processes are accelerated by a few drops of hydrochloric acid, the oxidation to a greater extent that the dimerization, and on long illumination the yield of α-truxillic acid diminishes and that of benzaldehyde increases. Cis-cinnamic acid behaves similarly, the yield of *β*-truxinic acid on long irradiation, especially in the presence of hydrochloric acid, decreasing as the result of the autoxidation of the cis-cinnamic acid. Here, too, the formation of β-truxinic acid is independent of the presence of admixed trans-cinnamic acid; both isomers polymerize, independently, to their dimers, even in suspension.

When the acid freshly prepared from the sodium salt of trans-cinnamic acid is illuminated in sunlight in hydrochloric acid suspension, it unexpectedly yields only *β*-truxinic acid and no α-truxillic acid.

[50] Chem. Abs. 1922, *16*, 2683.
[51] Chem. Abs. 1912, *6*, 2746.
[52] Chem. Abs. 1920, *14*, 58.
[53] Chem. Abs. 1921, *15*, 1888.

In connection with the stereoisomers of substituted ethylenes Stoermer [54] states that the conversion of the labile into the stable modification by the action of light, particularly in the presence of a halogen, is not uncommon. The converse change, produced by light alone, has been remarked in very few cases. Perkin has noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight, but Stoermer finds that in the coumaric acid series the tendency is the other way, the stable form changing to the labile under the influence of ultraviolet rays. Thus Perkin's change occurs only to the extent of 25 per cent, whereas coumaric acid yields 75 per cent of coumarin, methylcoumaric acid yields 75 per cent of methylcoumarinic acid, ethylcoumaric acid yields ethylcoumarinic acid quantitatively, and acetylcoumaric acid is also quantitatively changed to acetylcoumarinic acid. That the changes are caused by the ultraviolet rays is proved by means of light filters, the interposition of a filter which absorbs ultraviolet between the lamp and the solution preventing any change of the stable to the labile modification. Hence the less fusible stable forms of stereoisomeric compounds can be changed directly, under definite conditions, into the more reactive labile modifications if energy is supplied by ultraviolet rays. Thus the stable form of o-anisylcinnamic acid, which could not be changed into the labile modification by Stoermer and Frederici has been converted to the extent of 50 per cent by using a more intense radiation. In the case of stereoisomeric α-alkylated acids, the conversion of the stable into the labile form is a matter of great difficulty. The case of cinnamic acid is interesting. A benzene solution of ordinary cinnamic acid was exposed for eight days to the light of a uviol lamp, with the result that 25-30 per cent of Liebermann's isocinnamic acid, melting point 58°, was produced. Allocinnamic acid in benzene is converted into ordinary cinnamic acid under similar conditions. Also fumaric acid changes to maleic acid in eight days, but the conversion of mesaconic acid into citraconic acid is very difficult, these being α-methylated acids. When stilbene in benzene is exposed to ultraviolet for eight days, it is converted to the extent of about 90 per cent into isostilbene, which can be reconverted into stilbene by heating at 170-180° for one hour, by the vapor of fuming nitric acid in a few minutes, and quantitatively by the exposure to sunlight of its solution in carbon disulfide containing a trace of bromine.

According to Stoermer, Frederici, Brautigam and Neckel [55] the stable, less fusible forms of the following compounds are transformed into the labile or more fusible stereoisomers when their benzene or alcoholic solutions are exposed to the action of the ultraviolet rays from a uviol lamp for several days; coumaric acid, 75; methylcoumaric acid 75; ethylcoumaric acid over 90; propylcoumaric acid 85, methylcoumaramide, 50; ethylcoumaramide 100, propylcoumaramide 95; methyl coumarate; coumarin acetylcoumaric acid over 90; methyl benzoylcoumarate; methyl-o-nitro-o-methoxycinnamate 80; o-nitro-o

[54] Ber. 1909, *42*, 4865; J. Chem. Soc. 1910, *98*, *ii*, 114.
[55] Ber. 1911, *44*, 637.

methoxycoumaric acid 40, p-methoxycinnamic acid 25; sodium-o-chlorocinnamate 10; piperonylacrylic acid 17; maleic acid; o-anisylcinnamic acid 35-40; o-anisylcinnamide 70; o-anisylcinnam-methylamide 36; and the corresponding ethylamide 40; β-o-anisyl-α-methylcinnamic acid 5, and the corresponding amide 5; cinnamic isocinnamic acid, melting point 42°, 30-40; phenyl tolyl ketoxime, 40; phenyl anisyl ketoxime. In most cases the reaction is a balanced one, and the number given for each compound represents the percentage for the less fusible compound which has been transformed when equilibrium is established. Crotonic acid is not transformed to any appreciable ertent.

The method is recommended as a suitable one for the preparation of allo-stereoisomers in several cases and also for the detection of spatial isomerism between a pair of compounds. In a few instances the addition of methyl or ethyl alcohol to the unsaturated compounds occurs during the exposure to the ultraviolet but the amounts of such products are usually small. It is suggested that the transformation and the percentage amount transformed depend on the energy differences between the stereoisomers. Sodium fumarate is not transformed, although the corresponding acid yields 30 per cent of maleic acid. These investigators also state that o-chloro-cinnamic acid, or its sodium salt, when exposed to ultraviolet rays is partly transformed into the allo-acid, $C_9H_7O_2Cl$, but when glacial acetic acid solutions are used, part of the acid combines with acetic acid, giving a product, $C_{11}H_{11}O_4Cl$, melting point 212-213°. When a solution of mesaconic acid is subjected to the action of ultraviolet, water or methyl alcohol appears to combine with the acid. The change from one stereoisomeric form into another under the influence of radiation is frequently observed in the case of compounds containing an ethenoid linkage. In some instances ultraviolet rays produce changes which are the converse of those brought about by ordinary light.

Other examples in which acids combine with their solvents under the influence of ultraviolet radiation have been noted. Stoermer and Ladewig [56] discovered that when alcoholic solutions of trans-cyclopentane 1 : 2-dicarboxylic acid are exposed to ultraviolet (uviol lamp) conversion into mono- and di-esters occurs. The expected transformation into the cis-modifications did not occur. Benzoic acid is also esterified under these conditions (30 per cent in 8 days) and the reaction is still further promoted by the presence of a trace of hydrochloric acid (56 per cent in 8 days). Cinnamic acid is scarcely affected without the addition of a trace of hydrochloric acid, but the yield of ester may then reach 37 per cent in 8 days. The methyl esters of these acids were thus produced. Methyl salicylate becomes colored on exposure to air and sunlight, the tint varying from light yellow for short exposures to reddish-brown for protracted exposures. Gibbs, Williams and Pratt [57] observed similar results with o-, m- and p-cresols, the second of which colors most rapidly, while p-methoxytoluene was unaffected by light. The esters of the three hydroxybenzoic acids colored more rapidly than

[56] Ber. 1914, *47*, 1803.
[57] Philippine J. Sci. 1912, *7* (2), 79.

the free acids, the meta-compounds being the most rapidly changed, while the para-compounds were practically unaffected. Gentisic acid and its esters were found to be most susceptible to the action of light of all the substances employed. All the substances investigated, which become colored in sunlight, contain a labile hydrogen atom, and the behavior in sunlight is intimately connected with the absorption band in the ultraviolet, indicating ketoenolic tautomerism.

The effect of the rays from an iron arc on the hydrogenation of oleic acid is described by Custis.[58] The oleic acid was placed in a quartz flask which was fitted with a long air condenser and hydrogen gas was passed in. The arc was placed 1.5 centimeters from the flask and the exposure continued for 6 hours, when the degree of hydrogenation was determined by the iodine numbers. It was concluded that there was no acceleration in hydrogenation of oleic acid due to the action of the radiation, experiments performed without such exposure showing that the degree of saturation was practically equivalent in each case.

Drying oils, according to Marcusson,[59] when kept free from air in the daylight undergo an intramolecular polymerization, the iodine number drops, and the specific gravity is increased. Ultraviolet causes a more rapid polymerization. Chinese wood oil, in the absence of oxygen, forms a white mass, melting at 32° C. which cannot be considered a polymerized product. The fatty acids from this product melt at 71° C. and consist of β-eleostearic acid, an isomer of the α-eleostearic acid present in the original oil. The formation of β-eleostearic acid is similar to the transformation of allocinnamic acid into cinnamic acid in sterile storage.

Lesure [60] studied the penetration and chemical effects of a Cooper-Hewitt lamp of three amperes and 100 volts on solutions of 24 substances. In most of the solutions examined the penetration was as great as with water alone, but only 0.2 to 0.1 as great in the case of solutions of atoxyl, caffeine, salicylate of eserine, apomorphine hydrochloride, gentiopicrin and olive oil, and almost nil for mercury iodide, the bichloride and bisulfate of quinine and for iron methylarsinate. Solutions of silver nitrate, eserine salicylate, apomorphine hydrochloride, arbutin, and guaiacol were only slightly discolored, but without polarimetric change after an exposure of 15-30 minutes; while solutions of cocaine hydrochloride, mercury benzoate and bichloride, sodium cacodylate, calcium glycerophosphate, quinine bichloride (1%), pilocarpine hydrochloride and artificial serums were not affected upon exposure to the light for 30 minutes. Olive oil was bleached in less than half an hour, but not noticeably changed otherwise.

Compounds containing nitrogen are variously affected by exposure to ultraviolet. In some instances there is merely decomposition, while in others oxidizing effects are apparent. The formation of stereoisomers is common, and other rearrangements occur. Celluloid according to

[58] J. Frank. Ins. 1917, *184*, 880.
[59] Z. angew. Chem. 1922, *35*, 543.
[60] J. pharm. chim. *7*, 1, 569; Chem. Abs. 1911, *5*, 963.

Holmes and Patrick [61] when exposed to ultraviolet light becomes brown and brittle with the liberation of gaseous products, and not only adsorbed liquid but also the gel itself is decomposed by the rays.

Exposure to ultraviolet considerably accelerates the spontaneous decomposition of smokeless explosives, and this can be made the basis of a useful stability test. Explosives which were examined in this manner by Berthelot and Gaudechon [62] were cut into cylinders weighing 0.25-0.45 gram, placed over mercury in a quartz tube, containing nitrogen or carbon dioxide, and exposed to the radiation from a quartz mercury lamp at a distance of 78-80 mm. for 6 hours. In all cases rapid decomposition occurred with production of carbon monoxide or dioxide, nitrogen, and frequently nitrous and nitric oxides. Powders consisting only of nitrated cellulose were found to be more stable than those containing nitroglycerine. An English cordite containing 30 per cent of the latter and 5 per cent of vaseline, exposed in 1 c.c. of carbon dioxide, gave a mixture composed of the following volumes of gases: CO_2, 1 c.c.; CO, 0.17 c.c.; NO, 0.10 c.c.; N_2O, 0.02 c.c.; N_2, 0.10 c.c. Results are also given for the French A and B powders and for balistite of different ages and with stabilizers.

Experiments on smokeless powders were made by Berthelot and Gaudechon [63] in oxidizing (oxygen), reducing (hydrogen) and inert (carbon dioxide, nitrogen) atmospheres. With oxygen, two-thirds of the free oxygen disappeared and added its oxidizing effect to that of the oxygen of the nitrocellulose. With hydrogen, about one-quarter disappeared, forming water and formaldehyde. With carbon dioxide much depends on the temperature; at 25°-30° C. (70-80 mm. from the lamp) there is absorption, due no doubt to the solvents and stabilizers which are basic in their character; at 40° C. (50 mm. distance) no change in volume occurs; at 75° C. (20 mm. distance) there is disengagement of carbon dioxide from the powder and the final volume shows an increase. Nitrogen has no effect on the evolution of nitrogen or nitrous gases from the powder.

Nitroglycerine [64] 0.10 grams after 30 minutes exposure at 20 mm. gave 1.32 c.c. of gas containing carbon dioxide 24, carbon monoxide 10.5, nitrogen 17.5, nitrous oxide (N_2O) 8.5 and nitric oxide (NO) 39.5 per cent. Some nitric oxide was destroyed in attacking the mercury in the testing apparatus. The high percentage of nitric oxide explains its presence in the products of decomposition of powders containing nitroglycerine. A piece of nitrocellulose (collodion) 15 by 51.6 mm., after 2 hours at 20 mm., gave 0.87 c.c. of gas, the percentages of its constituents in the same order as above being 25.5, 19.5, 39, 7, 9. Collodion, though less nitrated than the French service smokeless powders, decomposes more readily and evolves a notable amount of nitric oxide. Comparison of two powders of the same age and make stabilized by amyl alcohol and diphenylamine respectively showed that at 20 mm.

[61] J. Phys. Chem. 1922, *26*, 25.
[62] Compt. rend. 1911, *153*, 1220.
[63] Compt. rend. 1912, *154*, 514.
[64] Compt. rend. 1912, *154*, 201.

(temperature 75° C.) amyl alcohol is the more efficient, the latter powder giving off less gas, and the gas containing a very much lower percentage of nitric oxide than the former. At 50 mm. (temperature 40° C.) on the other hand, diphenylamine is the more efficient stabilizer. Similar results were obtained with two more recently prepared naval powders, save that these evolved no nitrogen oxides. When the powders were treated with alkali (1 gm. with 20 c.c. of N/2 potassium hydroxide for 30 minutes at 15°) it was found that the diphenylamine powder showed less decomposition than that stabilized with amyl alcohol. A damaged naval powder, in which the brownish yellow plates showed whitish stripes, was examined by the lamp. At both distances the damaged parts gave off more gas than the unaltered parts, and this gas contained from 12 to 30 per cent of nitrogen oxides, while the gas from the unaltered parts contained none.

Piutti [65] notes that chloropicrin acts as an oxidizing, chlorinating, or nitrating agent, respectively, according to the compound with which it is exposed to light. With acetic acid, oxalic and chloroacetic acids are formed together with chlorine, hydrochloric acid, and nitrous acid. Similarly, with ethyl succinate, succinic acid; with methyl salicylate, methyl chlorosalicylate, oxalic acid, and ammonium tetroxalate; with toluene, benzoic acid, o-nitrotoluene, and oxalic acid, and with naphthalene, benzoic and phthalic acids are produced.

On exposure to ultraviolet rays [66] urea is converted first into ammonia and then into nitrite. Other organic nitrogen compounds—e.g. ethyl and methylamine, guanidine, hydroxylamine, acetamide, acetonitrile, etc., behave similarly. Stress is laid on the close analogy between the effects of the rays and the action of enzymes.

Berthelot and Gaudechon [67] have compared the effectiveness of different ultraviolet rays in the photochemical synthesis of quaternary compounds in the polymerization of different gases and in the photolysis of acetone. Equal volumes of carbon monoxide and ammonia combine in a few hours to give formamide under the influence of the ultraviolet rays (2000 Å) from a quartz mercury lamp. Combination also takes place slowly with medium ultraviolet rays (2000-3000 Å), but there is no combination under the influence of initial ultraviolet or solar rays longer than 300 μμ (3000 Å).

On the other hand, formamide slowly decomposes when submitted to ultraviolet rays, the reaction being complicated by dehydration and formation of hydrogen cyanide. Light, less markedly than heat, produces polymerization.[68] Cyanogen exposed to sunlight slowly polymerizes. In the presence of oxygen and ultraviolet, it is oxidized practically completely to carbon dioxide and nitrogen. A carbon tetrachloride solution of thiocyanogen $(SCN)_2$, according to Kaufmann and Liepe,[69]

[65] Atti. I. Congr. naz. Chim. pur. appl. 1923, 437; Chem. Zentr. 1924, i, 2514; see also J. Chem. Soc. 1921, *120, i,* 298.
[66] Compt. rend. 1911, *152,* 522.
[67] Compt. rend. 1912, *155,* 207.
[68] Compt. rend. 1910, *150,* 1164.
[69] Ber. 1923, *56 B,* 2514.

polymerizes readily in the sunlight. In ethereal solution substances having powerful odors are formed.

Blanksma [70] has noted that acetylchloroaminobenzene is altered by light, following the general rule that the radicals Br, Cl, NO_2, NO and O attached to nitrogen, change places, under the influence of sunlight, with a hydrogen atom in the nucleus. Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight.[71] The compound has attracted considerable attention in connection with the theory of solutions. With dilute hydrochloric acid the compounds R·CO·NR·Cl undergo a molecular rearrangement in which the chlorine attached to the nitrogen exchanges places with one of the hydrogen atoms of the benzene ring. This reaction may be represented as follows: $CH_3CONClC_6H_5 + HCl = CH_3CONHC_6H_4Cl + HCl$. When a solution of the compound is exposed to ultraviolet, the rearrangement takes place without the aid of the mineral acid catalyst.

Mathews and Williamson [72] have studied this action in benzol, alcohol and acetic acid as solvents, using a quartz mercury lamp. The solvent is found to have a marked effect on the behavior of the reaction. When water is added to an alcoholic or glacial acetic acid solution of acetylchloroaminobenzene, the velocity of the photo-decomposition is greatly diminished. It also causes the reaction to proceed as a true photochemical reaction, whereas in the absence of water the reactions in absolute alcohol and glacial acetic acid solutions proceed without the action of radiation after having been started thereby.

Diazocamphor prepared from inactive amino-camphor as well as that prepared from the dextro compound are decomposed in benzol solution by light of wave-length 220-300 μμ (2200-3000 Å), but visible light has almost no action.[73] Inactive lactic acid is decomposed by light of wave-length 220-300 μμ (2200-3000 Å) but is not rendered optically active.

Bass [74] has found that when aqueous solutions of thymine, in an atmosphere of oxygen are irradiated by a quartz mercury arc, some urea and pyruvic acid are formed, but no acetol. Ferrous sulfate and, to a less extent, potassium ferrocyanide catalyze the reaction. In an atmosphere of nitrogen no split occurs, even in the presence of the above named catalysts.

On exposing solutions of the semicarbazones of dypnone and phenyl β-phenylstyryl ketone, and the mesityl oxide α-phenyl semicarbazones to a quartz mercury lamp, Wilson and Macaulay [75] found that stereoisomers were formed. Attempts to prepare stereoisomers of the semicarbazones of benzylactone, benzyl acetophenone, methyl styryl ketone, and styryl isobutenyl ketone gave negative results.

[70] J. Chem. Soc. 1902, *82*, 646.
[71] J. Chem. Soc. 1902, *81*, 200.
[72] J. Am. Chem. Soc. 1923, *45*, 2574.
[73] Mangold and Williams, Z. Angew. Chem. 1923, *36*, 456; Chem. Abs. 1923, *17*, 3868.
[74] J. Am. Chem. Soc. 1924, *46*, 190.
[75] J. Chem. Soc. 1924, *125*, 841.

Muffat and Heitz [76] note a reaction whereby 1-phenylpyrazolines are obtained by the action of phenylhydrazine on certain aromatic ketones, owing to the extraordinary ease with which the hydrazones first formed rearrange.

Ciamician and Silber [77] showed the nitrobenz*anti*aldoximes are changed into the corresponding *syn*-isomers when their benzol solutions are exposed in glass tubes to the sunlight. *p*-chloro- and 3 nitro-p-methoxy-benz*anti*aldoximes are likewise converted according to Ciusa,[78] but no isomeric change occurs under these conditions in the case of benz*anti*aldoxime and 3, 4-methylenedioxy*anti*aldoxime. He infers that the presence of a negative substituent is necessary for the transformation to take place. In more recent work Brady and McHugh [79] used a quartz mercury vapor lamp. Twenty-four aldoximes and derivatives were submitted to the action of ultraviolet.

It has been found that *p*-methoxy- 3:4-methylenedioxy-benz*anti*-aldoximes and benz*anti*aldoxime are all converted into the *syn*-isomerides. The quartz mercury vapor lamp is a convenient means for bringing about the conversion and, in addition to the three oximes above mentioned, *o*-, *m*-, and p-nitro-, *o*-, *m*-, and *p*-chloro-benz*anti*aldoximes have been transformed into the corresponding *syn*-derivatives.

With two exceptions, all the aldoximes investigated which had previously been obtained in two isomeric forms were almost completely converted into the *syn*-isomerides. The exceptions were 5-bromo-3:4-dimethoxybenz*anti*aldoxime [80] which suffered demethylation, giving 5-bromo-3-methoxy-4-hydroxybenz*anti*aldoxime, and 3:4-dimethoxy-benz*anti*aldoxime, which underwent no change, although Brady and Dunn [81] have obtained the *syn*isomeride under special conditions.

Eight aldoximes were investigated which cannot be converted into *syn*-isomerides by any of the usual methods, namely, (1) *o*-methoxy-, (2) 5-bromo-*o*-methoxy-, (3) 2:4-dinitro-, (4) 3-nitro-*p*-dimethyl-amino-, (5) 6-nitro-3 : 4-methylenedioxy-, (6) 5-nitro-3 : 4-dimethoxy-, (7) 6-nitro-3 : 4-dimethoxy-, and (8) 5-bromo-3-methoxy-4-hydroxy-benz*anti*aldoximes. So far, the only derivatives which have been investigated are a number of ethers. The methyl ether of benz-aldoxime is decomposed by ultraviolet with the formation of benzonitrile, while the methyl ether of *m*-nitrobenzaldoxime undergoes no change. The methyl ethers of *m*- and *p*-nitrobenz*anti*aldoximes are partly converted into the corresponding *syn*-isomerides; this confirms the results previously obtained on the action of sunlight on these compounds.[82] The o-benzyl ether of p-nitrobenz*anti*aldoxime was converted into the *syn*-isomeride. It is concluded that, in the case of the aromatic aldoximes, conversion by the action of ultraviolet is possible only when the two isomerides can be prepared by the usual methods and that the

[76] Ber. 1918, *51*, 1457.
[77] Ber. 1903, *36*, 4268.
[78] Atti. R. Accad. Lincei. 1906 (v), *15*, *ii*, 721.
[79] J. Chem. Soc. 1924, *125*, 547.
[80] See Wentworth and Brady, J. Chem. Soc. 1920, *117*, 1040.
[81] J. Chem. Soc. 1923, *123*, 1790.
[82] J. Chem. Soc. 1913, *103*, 1624.

presence of negative groups is not essential as stated by Ciusa. A sufficient number of ethers has not been examined to enable any conclusion to be drawn, but it appears that the conversion does not take place so readily or so completely as with those oximes which undergo change.

Custis [83] reports the following experiments on trinitrotoluene. The compound was placed in a capillary tube made of quartz. This tube was kept in the path of the rays emanating from an iron arc which was placed 1.5 centimeters from the tube. After six hours' exposure the product was examined; it had turned a dark brown. Samples of trinitrotoluene, melting point 80.47°, were placed, one in a capillary tube made of quartz, and another in a capillary tube made of glass. These tubes, together, were placed on a table 7 centimeters from a mercury quartz lamp. The heating effect of the lamp on the tubes was greatly reduced by employing a mechanical blower, so arranged as to drive a constant stream of air over the tubes. The temperature indicated by the thermometer was 30° at the beginning and 40° at the end of a three-hour period. After an exposure of the above duration the samples were examined. There appeared to be no darkening of the crystals in either tube. The melting point of both specimens was found to be the same, namely 80.21°. This identity in the change of melting point in samples contained in glass and quartz, and exposed to the rays from a quartz mercury arc, seemed surprising. The experiments indicate that artificial light does not materially affect trinitrotoluene, and that the long ultraviolet rays (i.e., those which can pass through 7 centimeters of air) have little, if any, greater effect than the visible rays from a quartz mercury arc. The change in this nitro compound is stated to be due to oxidation. Trinitrotoluol, 2,4,6, darkens in light, forming a red coloring matter, the effect being about the same on exposure either to sunlight or ultraviolet rays. The coloration is ascribed by Schultz and Ganguly [84] to the formation of a quinone oxime derivative.[85]

Ultraviolet rays have been employed by Bass and Johnson [85a] in the determination of the action of nitrogen peroxide on toluene, as follows:

> Twelve g. of toluene and 2.5 g. of nitrogen peroxide, in a sealed ampule, were allowed to stand in a dark closet for 3 months. At the end of this time the color of nitrogen peroxide had disappeared, the liquid had become yellow and a very small quantity of a yellow solid had deposited. The reaction mixture returned 7.6 g. of unaltered toluene and 4.1 g. of a crystalline substance which was identified as benzoic acid. There was no evidence of the formation of a nitro derivative.
>
> 2. Anhydrous nitrogen peroxide gas in excess was passed over 50 g. of dry toluene in a transparent quartz tube. During this operation, which was continued for 4 hours, the tube was irradiated by means of a quartz mercury arc, and the temperature of the toluene did not rise above 55°. On distillation a

[83] J. Frank. Inst. 1917, *184*, 876.
[84] Ber. 1925, *58B*, 702.
[85] Note also Molinari and Giua, Escales, Nitrosprengstoffe, 295; Custis, Chem. Trade Jour. *62*, 90; Centralblatt 1919, I, 208.
[85a] J. Am. Chem. Soc. 1924, *46*, 456.

small quantity of a low-boiling liquid (which decomposed on standing at ordinary temperature with slow evolution of nitrogen peroxide and unaltered toluene) was obtained.

3. The experiment described above was repeated with the same quantity of toluene but with the substitution of a water-cooled quartz reaction tube. The duration of the irradiation was increased to 6 hours. On distillation the reaction mixture yielded 13.0 g. of the unstable low-boiling liquid (40-80°), 32.0 g. of toluene, and 2.5 g. of a crystalline solid which consisted almost entirely of benzoic acid.

The low-boiling liquid (40-80°) on redistillation showed no definite boiling point, but gradually decomposed with the formation of pure toluene and liberation of nitrogen peroxide in large quantity. This product appears to be an unstable addition product of the peroxide and toluene. In this case, therefore, the nitrogen peroxide acted as an oxidizing reagent and practically no nitration took place.

Baudisch and Furst [86] have arrived at the following conclusions as the result of photochemical experiments. The change produced by light on the ammonium salt of alpha-nitrosonaphthylhydroxylamine is due to the action of violet and blue rays of comparatively long wave-length which will pass through glass and other substances. If a piece of stout filter paper be treated with the above salt, steamed, and exposed to the rays from a quartz mercury vapor lamp with a glass plate covering half of the sheet, it is found that the paper is uniformly reddened. The same result is obtained by using a gelatin plate or a solution of starch or albumin. If, however, the filter paper is treated with a solution containing potassium nitrate or potassium iodide and starch and irradiated in the same way, it will be found to turn blue only where it is uncovered. The rays which cause the evolution of oxygen from potassium nitrate are of short wave-length and are absorbed by various filters. It is suggested that the colloids of plant cells can exercise a similar differentiating influence on the radiation which they receive. From the above ammonium salt, free alpha-nitrosonaphthylhydroxylamine can easily be obtained by precipitation with metaphosphoric acid. It is soluble in chloroform but the solution gradually changes owing to the reducing action of the chloroform, which forms *a*-diazo naphthalene chloride.

The effect of ultraviolet rays on nicotine and pyridine has been studied by Custis,[87] who found that ultraviolet radiation produces a change in nicotine solutions. A 0.1 per cent solution of nicotine when exposed in a quartz flask at 5 centimeters from a source of ultraviolet for 15 minutes showed a decided decrease in nicotine content. A 40 per cent solution of commercial nicotine, when exposed for 30 minutes at 5 centimeters from an iron arc showed an increase in the amount of nicotine present. Custis explains this increase in the second sample on the grounds that commercial nicotine contains impurities in the form of certain oils and it is not unlikely that nicotine was synthesized from these oils.

Phenolphthalein is reduced to phenolphthalin by the action of nascent

[86] Ber. 1912, *45*, 3426.
[87] J. Frank. Inst. 1917, *184*, 878.

hydrogen, according to Rossi,[88] while the reverse reaction takes place in the presence of hydrogen peroxide, and may be employed for the detection of blood. In the absence of the latter, the oxidation proceeds very slowly and may take days, but when blood is present the action is much more rapid. The test is carried out as follows: An alkaline solution of phenolphthalein is shaken with zinc dust until colorless, filtered, and the filtrate mixed with the solution to be tested, to which a few c.c. of 12 per cent hydrogen peroxide have been added previously. If blood is present, a red coloration develops within three hours. Exposure to bright light, such as an arc-light, also increases the rapidity of the oxidation of phenolphthalin.

Piutti[89] states that the transformation of santonin into photosantonic acid and isophotosantonic acid by light proceeds by way of intermediate compounds. Photosantonic acid and probably also isophotosantonic acid are very transparent to the ultraviolet rays, but santonin is not. No confirmation could be obtained of the alleged re-conversion of yellow santonin into white on boiling. The alleged visible alteration of santonin crystals under radiation could not be observed.

A study of the reaction between chromic acid and quinine has been made by Goldberg,[90] whose results seemed to indicate that the velocity was dependent on the extent to which the rays are absorbed by the chromic acid. Luther and Forbes[91] have found, however, by means of monochromatic radiation, that the quinine is the substance which is sensitive, while the chromic acid only acts as an indifferent ray filter, absorbing a part of the rays and converting these into heat. The source of radiation was a uviol mercury vapor lamp, and a series of filters were employed. It was found in preliminary experiments that the total reaction velocity was proportional to the concentration of the hydrogen ion. The photochemical reaction is exactly the difference between the total reaction and the spontaneous reaction of the same mixture in the dark, and the combined effect of the velocities is additive. The speed of the photochemical reaction is proportional to the quantity of rays of given wave-length absorbed by the quinine alone unless the concentration of the chromic acid is very small. It is probable that the reaction takes place in two stages: (1) the formation of sensitized quinine with a velocity proportional only to the ray absorption, and (2) a reaction in ordinary sense, between this product and chromic acid with a velocity proportional to the concentration of the chromic and sulfuric acids. By applying the results to the data obtained by Luther and Forbes[92] in the investigation of the photochemical oxidation of quinine by chromic acid, it is found that the ratio of the intensities of the bands λ 406 $\mu\mu$ and λ 362 $\mu\mu$ (4060 and 3620 Å) is 1.00 : 0.75, which is in good agreement with the corresponding ratio of the velocity-coefficients, 1.00 : 0.82.

[88] Chem. Zentr. 1911, *82, ii,* 1659; Giorn. Farm. Chim. 1911, *60,* 433; J. Chem. Soc. 1912, *102, ii,* 107.

[89] Att. R. Acad. Lincei, 1913 (V), *22, ii,* 92.

[90] J. Chem. Soc. 1906, *90, ii,* 514.

[91] J. Amer. Chem. Soc. 1909, *31,* 770.

[92] J. Chem. Soc. 1909, *96, ii,* 632.

This would seem to show that the reaction velocity is proportional to the absorbed energy, and independent of the frequency of the light. When an aqueous solution of quinine sulfate in contact with air is exposed to the rays emitted by a quartz mercury vapor lamp, oxygen is absorbed. Weigert [93] has made experiments directed to an explanation of the nature of this reaction. The progress of the change could be readily followed by measurements of the volume of gas absorbed.

The reaction velocity increases with increasing concentration of the quinine sulfate, but is diminished by addition of acid. From experiments with gas mixtures containing variable proportions of oxygen, it is found that the reaction velocity increases continuously as the partial pressure of the oxygen diminishes. For a mixture of oxygen and nitrogen containing 0.6 per cent of oxygen, the velocity is about thirty times as large as for pure oxygen. The nature of the oxidation process appears to vary, however, with the proportion of oxygen in the gas mixture, for a larger proportion of the absorbed oxygen was found to have been activated when the gas mixture was rich in oxygen. The activated oxygen is only present to a small extent in the form of hydrogen peroxide, the major portion existing in a loosely combined form, which may be removed by a current of carbon dioxide or nitrogen. A similar influence of the oxygen concentration on the reaction velocity has also been observed in the photochemical oxidation of fluorescein and tetraiodofluorescein. When air is passed through isoeugenol in which is immersed a lamp emitting ultraviolet rays vanillin is formed.[94] The theory of the operation is that the ultraviolet converts oxygen in the air to ozone and this in turn is responsible for the oxidation. It will be seen at once that the rate of oxidation depends upon the penetrating power of the rays, and this in turn is dependent upon the clearness of the isoeugenol. The use of distilled isoeugenol, which is much more expensive, is therefore necessary. Even starting with a very light colored product, the oil darkens in a couple of hours so that the rate of oxidation rapidly decreases. Another difficulty in this process arises from the fact that, under the conditions of the tests, the air was circulated through the solution at a rate of about 30,000 cu. ft. per hour, and this caused a considerable loss of isoeugenol by vapor tension. When using 30,000 cu. ft. of air per hour on 800 lb. of isoeugenol the loss amounts to about 80 lb. in 8 hours. Genthe and Company [95] also propose the oxidation of eugenol by means of air in the presence of ultraviolet rays. The air is passed through the eugenol maintained at 50°-60° C. and the yield of vanillin is stated to be as high as 95 per cent.

The spontaneous transformation of solutions of odorous substances to a colloid state by exposure to ultraviolet has been investigated by Zwaardemaker and Hogewind.[96] A number of solutions of odorous

[93] Festschrift W. Nernst. 1912, 464; J. Chem. Soc. 1912, *102*, ii, 1120.
[94] Wood, Chem. & Met. Eng. 1923, *28*, 399.
[95] German Patent 224,071.
[96] Proc. K. Akad. Wetensch. Amsterdam 1918, *21*, 131; J. Chem. Soc. 1919, *116*, ii, 14.

substances in water, glycerol, or paraffin are found after keeping for several weeks to have passed into the colloidal condition. The action is much more rapid in daylight than in the dark, while in the presence of ultraviolet the action is still more rapid. In the case of many substances the transformation occurs only in the presence of ultraviolet, the colloid particles being negatively charged. Among others, the following substances were examined: eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol and hypnone. Triglycerides are hydrolyzed by subjecting them in the presence of water, to the action of ultraviolet rays at the ordinary temperature and pressure.[97]

Kailan [98] has investigated the action of radium rays on chloroform and carbon tetrachloride, and has compared the effect produced with that obtained by ultraviolet rays. The ultraviolet rays are more active than the radiation of radium. The chloroform becomes turbid and increases in density. Hydrochloric acid, hexachlorethane and an amorphous reddish brown solid can be detected in the liquid.

A number of substances, when exposed to light, undergo a change in color, but again revert to their original hue when left in the dark. To designate such phenomena, Markwald [99] has applied the term phototropy. The characteristics of phototropic transformation are briefly considered by Gallagher,[100] and various explanations of the phenomenon already proposed are stated as follows: (a) Polymorphism, (b) the formation of stereoisomers, (c) the formation of physical aggregates of the products of chemical polymerization and (d) intramolecular changes. This study indicates no direct relation between phototropy and chemical constitution, and it is not justifiable to attribute the changes of color to the purely chemical alterations in the molecule.

Fulgides, containing aromatic substituting groups, are reported by Stobbe [101] to undergo change in color when exposed to light. Thus triphenylfulgide, which forms pleochroic, orange-red, monoclinic crystals, becomes dark brown when exposed to sunlight or the rays of an arc lamp, changing again to its original color in the dark. The brown and orange modifications are chemically identical, and differ only in the solid state. If this phototropic change is frequently repeated, the difference between the shades of the two forms becomes gradually less, a chemical change taking place which leads finally to the complete conversion of the fulgide into a new substance, the photoanhydride. To study the action of light waves of different lengths, the fulgide is exposed in a thin layer between two glass plates in a special spectrographic apparatus. Orange-yellow triphenylfulgide, when exposed to the light of the spectrum, after two minutes shows a broad band between the spectrum lines E and G, which after prolonged exposure gradually extends towards the ultraviolet. The yellow modification is

[97] German Patent 357,695; J. S. C. I. 1922, *41*, 945 A.
[98] Monatsh. 1917, *38*, 537; J. Chem. Soc. 1918, *114*, *i*, 209; Chem. Abs. 1918, *12*, 2196.
[99] Z. Physikal. Chem. 1899, *30*, 140.
[100] Bull. soc. chim. 1921, *29*, 683.
[101] Annalen 1908, *359*, 1; J. Chem. Soc. 1908, *94*, *ii*, 339.

sensitive to blue and violet light rays, but a blackish-brown form which is intermediate between the yellow and brown modification is sensitive to yellow and red rays. The portion of the spectrum which causes the phototropic change from the yellow into the brown modifications is termed the zone of stimulation. The behavior of a number of di- and tri-arylfulgides towards the light rays of different wave-lengths has been studied in this manner. Phototropic change has been observed only with the lemon-yellow to orange-red diaryl—and the orange-red to dark red triarylfulgides; the colorless alphyl, greenish-yellow to yellow monoaryl, and red, purple-red, or brown or tetraarylfulgides are not phototropic.

The modifications of a phototropic substance can exist in the pure state only when exposed to light rays of the wave-length under the influence of which they are formed. Under all other conditions, the substance is a mixture or solid solution of the one form in the other. The phototropic change is caused by the light rays which are absorbed by the modification undergoing the change. Hence the brown form of triphenylfulgide must be in reality blue, the brown appearance resulting from its state of granulation. The equilibrium between the two modifications in a mixture depends on the wave-lengths of the light to which it is exposed. It follows that the parts of the spectrum which produce the phototropic change depend on the color of the fulgide, the zone of stimulation lying the more towards the violet the deeper the normal shade of the substance, and that the amount of change in the color of a phototropic fulgide not only increases with diminishing wave-lengths of the light rays and with increasing intensity of illumination, but diminishes with increasing temperature and depends, further, on the number and nature of the substituting groups, being greatest with diphenyl-o-methoxyphenyl-, diphenyl-piperonylallo-, and diphenyl-o-nitrophenylfulgides, less with diphenyl-o-methoxyphenylfulgide, and least with the diarylfulgides. The furyl-fulgides resemble the phenyl compounds.

Heilbron and Wilson[102] have shown that cinnamaldehydesemicarbazone exhibits a type of phototropy which is the converse of that ordinarily observed. When first prepared, it is colorless, and, if immediately placed in the dark, undergoes no change of color. If, however, the semicarbazone is exposed to diffused sunlight for some hours, although no visible effect is noticeable, on now placing it in the dark, a yellow color develops on the exposed surfaces, which again disappears on re-exposure to light. This phenomenon, which is designated as *reversed* phototropy, has been further studied by Heilbron, Hudson and Huish.[103]

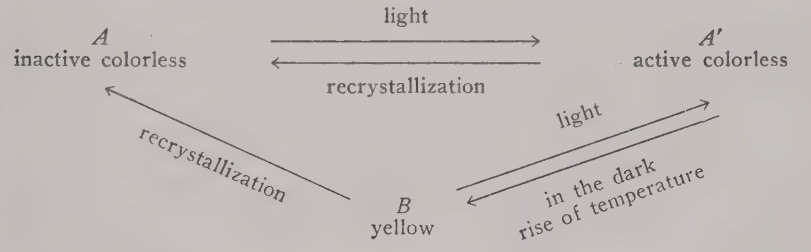
The methoxycinnamaldehyde-semicarbazones and -phenylsemicarbazones all crystallize from solution as colorless substances, and, with the exception of m-methoxycinnamaldehyde-diphenylsemicarbazone, which is insensitive to either sunlight or ultraviolet, all exhibit reversed phototropic properties. On the other hand, the thiosemicarbazone derivatives, which may be expected to be quite similar in character, exhibit only

[102] J. Chem. Soc. 1914, *105*, 2892.
[103] J. Chem. Soc. 1923, *123*, 2273.

direct phototropy, becoming yellow in diffused sunlight and not reverting to the colorless modification on removal from the source of light. A series of experiments has been carried out with the view of obtaining evidence of phototropic change in solution, and for this purpose solutions of the intensely phototropic o-methoxycinnam-aldehyde-thiosemicarbazone in various solvents were exposed for lengthy periods to sunlight. In no case, however, was there the slightest indication of the production of any color in the solution and it may thus be reasonably concluded that phototropy is essentially a characteristic of the solid state.

The phenomenon of thermotropy is very strikingly manifested by the semicarbazones exhibiting reversed phototropy. So long as any of these remain unactivated by light, rise in temperature produces no color change. On the other hand, after exposure to sunlight, in certain cases even for so short a period as five minutes, the colorless activated substance becomes yellow almost immediately when placed in a steam-oven.

It will be seen that in a reversed phototropic change the first effect must be one involving the absorption of a certain number of energy quanta, whereby the molecule is transformed from its inactive, colorless phase (A) into an *active* colorless variety (A′). This latter form is in turn transformed into the colored modification (B), phototropic equilibrium being established between the latter two phases:



Stobbe has shown that in the case of the fulgides [104] the active wavelengths involved in the bringing about of *direct* phototropic change are those which the substance itself absorbs. As indicated below, this applies equally in the present series. An ordinary photographic plate was fixed, washed, and when almost dry dusted over with colorless, inactive cinnamaldehydesemicarbazone. The plate was then placed in the spectrograph and exposed for about two hours, an iron arc being used as source of radiation. On examining the semicarbazone, no visible change was detected, but after leaving the plate over night, a narrow, yellow band was clearly indicated at 280 μμ (2800 Å), this being the characteristic ultraviolet frequency of the substance.

In order to determine whether energy is emitted during the transformation in the dark of the active colorless into the colored form, a photographic plate covered with cinnamaldehyde-phenylsemicarbazone was activated in strong light and then placed in the dark in contact with an undeveloped plate. After being left over night, during which time

[104] J. Chem. Soc. 1923, *123*, 2273.

the phenylsemicarbazone had become yellow, the upper plate was developed, but no mark whatsoever could be detected on it.

Heilbron, Hudson and Huish believe that a phototropic change simply represents an intermediate stage of an irreversible chemical reaction. The active phases of higher energy content which are similar to Baly's activated molecules [105] would tend either to lose energy and again pass into the inactive phase (recrystallization effect), or, on the other hand, to undergo complete chemical change with formation of a new substance. Thus Stobbe [106] has found with the fulgides, that, when the phototropic change is frequently repeated, the difference of color between the two forms becomes gradually less, the phototropic process giving place to a non-reversible chemical reaction in which a substance of different constitution is produced. Similarly, Halban and Geigel [107] have shown that, in the case of tetrabenzoylethylene, an irreversible chemical change rapidly follows the primary phototropic process.

The phototropy of other substances has also been studied by Stobbe.[108] The zone of stimulation for colorless β-tetrachloro-α-ketonaphthalene lies in the ultraviolet, while the reverse change is caused by yellowish-green or yellowish rays. Red and blue rays have no action.[109]

Phenylbenzylidenehydrazine, which forms light yellow crystals or a white powder, becomes red on exposure to violet or ultraviolet rays, becoming again colorless when exposed to yellow or green light. Phenylanisylidene- and phenylcuminylidenehydrazines behave in the same manner, as do also osazones of the benzil series.[110] Tetraphenyldihydrotriazine [111] and ethyl oxalisobutyrate [112] have also been observed to exhibit phototropy.

The rays of the quartz mercury lamp, according to Gibbs,[113] color pure phenol, in the presence of oxygen, with remarkable rapidity. Samples exposed in small dishes covered with quartz plates are colored light red after an exposure of one minute.

Cumming and Steel [114] isolated two modifications of α-azoxynaphthalene in yellow plates and red rhombic crystals, both melting at 127°. The yellow modification is phototropic, being converted into the red modification on exposure to bright sunlight for a few minutes or to ultraviolet rays. Very sharp prints were obtained by exposure of paper, moistened with a very dilute alcoholic solution of the yellow modification, to sunlight behind a photographic negative. The modification is ascribed to a change in structure from RN-O-NR to O : NR : NR.

[105] Phil. Mag. 1920 (vi), *40*, 15.
[106] Loc. cit.
[107] Z. physikal. Chem. 1920, *96*, 233.
[108] Loc. cit.
[109] See also Stobbe, Ber. Verhandl. Sächs, Akad. Wiss. Leipzig 1922, *74*, 161; Chem. Abs. 1923, *17*, 3020.
[110] Biltz and Wienands, J. Chem. Soc. 1899, *76*, 910.
[111] Walther, J. Chem. Soc. 1903, *84, i*, 592.
[112] Wislicenus and Kiesewetter, J. Chem. Soc. 1898, *74, i*, 240.
[113] J. Am. Chem. Soc. 1912, *34*, 1193.
[114] J. Chem. Soc. 1923, *123*, 2464.

An interesting photochemical method of detecting ultraviolet rays has been described by Schall.[115] A sheet of paper is floated on a solution of one part by weight of p-phenylene diamine in 14 parts of water and 4 parts of a 40 per cent solution of nitric acid. The paper is dried by heating and used at once. Diffused daylight produces only a pale gray tint, but an instant's exposure to the ultraviolet rays from a quartz mercury lamp produces a blue coloration. Schall[116] also notes that paper prepared with *p*-phenylenediamine nitrate (2/3 normal) is sensitive only to waves shorter than 313 μμ. As the solar spectrum ends at about 295, the paper is suitable for determining the variations (e.g., with altitude) of the solar radiation of short wave-length and has been used for this purpose.

Schall[117] finds that test paper (which turns blue in ultraviolet, but does not alter in diffused daylight) may be used to show differences of absorption in the ultraviolet as follows. A trough, the front and back of which are made of transparent quartz, is partly filled with alcohol, and along with a second (empty) trough of glass is set up in front of a sheet of the test paper in question. The troughs and paper are then exposed. After a few minutes, white silhouettes of the troughs on a blue background are observed on the paper. Where the rays of the short wave-length meet air, alcohol, or quartz they penetrate sufficiently to produce color. If instead of alcohol, a concentrated solution of naphthalene in the latter solvent is used in the quartz trough, a completely white image of the trough is obtained, as naphthalene absorbs the ultraviolet rays.

The leuco-bases of Brilliant Green, Malachite Green, Crystal Violet, Rhodamine B, 3 B and 6 G, also leucaniline and "leuco blue," are sensitive to the respective complementary colors of the dyes and may be used for actinometric purposes. Mixed with collodion they are more light-sensitive than the dyed silver bromide and silver chloride films hitherto used in photometry. As it is sensitive to ultraviolet, according to Eder[118] the leuco-base of Brilliant Green is specially suited for use in plant physiology experiments, being sensitive to that part of the spectrum which is active in chlorophyll formation. Free halogens are the toxic substances in the experiments described by Clark[119] with eosin and erythrosin. A simple photochemical reaction has been developed by Lifschitz[120] from the well known behavior of triphenylmethane dyes which, when treated with potassium cyanide, pass over into the colorless

[115] Photograph. Wochenblatt 1907, *33*, 321.
[116] Chem. Ztg. 34, 267.
[117] Zeitsch. physikal. Chem. Unterr. 1908, *21*, 389. Mott and Bedford, J. Ind. Eng. Chem. 1916, *8*, 1029, made paraphenylenediamine test paper as follows: white blotting paper was impregnated with this compound in nitric acid solution (1 gram of paraphenylenediamine, 3 c.c. distilled water, 2 c.c. nitric acid, specific gravity 1.21). The blotting paper was then dried in a steam oven for about one-half hour.
[118] Phot. Korr. 1919, *56*, 140; Chem. Zentr. 1919, *90*, IV, 396; J. S. C. I. 1919, *38*, 878 A.
[119] Amer. J. Physiol. 1918, *47*, 251.
[120] Ber. 1919, *52*, 1919.

triarylacetonitrile. On exposure to ultraviolet the color of the solution is restored, but slowly disappears again when placed in a dark room.

A method employed by DeWierusz-Kowalski [121] to bring about the condensation of organic compounds, such as a mixture of acetone and methyl alcohol, consists in conducting the mixed vapors under reduced pressure through hollow bodies which are in a high frequency field, in such manner that these vapors themselves act as carriers for the luminescence.

In treating liquids with ultraviolet rays [122] the liquids to be exposed are sprayed into a series of vertical tubes by means of compressed air or steam. These tubes are arranged about a lamp emitting ultraviolet rays and have their lower ends connected with a collecting vessel. In another form of apparatus the liquid is sprayed directly into a chamber containing the lamp. Oil, or oil mixed with oxygen may be treated in this manner to secure a bleaching effect.

A photochemical apparatus is described by Snelling [123] in which the reacting fluids are caused to pass through a series of transparent vessels, each of which has a source of light opposite to it, the distance between the source of light and the reaction vessel being decreased progressively in the direction of flow of the fluids. Chemical reactions are carried out by Brutzkus [124] in the interior of a compressor under such conditions that the reacting substances are first brought to a suitable temperature and pressure either by compression or expansion, and then caused to react while maintaining the temperature and pressure substantially constant. In the production of ozone, oxygen is compressed and during the remaining part of the compression stroke is subjected to "induction sparks," silent discharges, or ultraviolet rays, the gases being released at the end of the compression stroke in order to prevent the decomposition of the ozone. The ozone so obtained may be employed *in situ* for effecting oxidation.

[121] French Patent 466,918, Dec. 8, 1913.
[122] Wierusz-Kowalski, French Patent 468,216, Feb. 5, 1914.
[123] J. S. C. I. 1920, *39*, 476 A; U. S. Patent 1,339,675.
[124] British Patent 155,776, Dec. *22*, 1920; Chem. Abs. 1921, *15*, 1585.

Chapter 10.

Effect of Ultraviolet Radiation on Halogenation Reactions.

Visible light of short wave-length and ultraviolet rays have long been employed to assist in reactions involving halogenation. With the exception of fluorine, the halogens, or their compounds, afford many instances where modification takes place under the stimulus of such radiation. The stability of fluorine and the fluorides in light of all wave-lengths tested thus far is in keeping with their chemical behavior in general. Chlorination of toluol in light to make benzyl chloride, benzal chloride and benzotrichloride and by hydrolysis benzyl alcohol, benzaldehyde and benzoic acid therefrom is a procedure of long standing, one in fact which has received considerable commercial use. The chlorination of methane (natural gas) to obtain carbon tetrachloride and chloroform represents another development. War-time demands and liquor prohibition created a scarcity of amyl alcohol (fusel oil) which heretofore was used to a large degree in the production of nitrocellulose coating compositions. This stringency resulted in extensive investigations to chlorinate butane, pentane and hexane to form monochlor compounds which in turn could be converted into the corresponding alcohols or acetates. Commercial developments in progress were arrested by the perfection of a process of making primary butyl alcohol by fermentation. This product proved acceptable to manufacturers of nitrocellulose lacquers. Secondary alcohols are now made commercially from the olefins of cracked petroleum (pressure still gases) by a process developed in the laboratory of the senior author, involving the formation of alkyl hydrogen sulfate and subsequent hydrolysis to yield the alcohol. These methods have tended greatly to diminish the importance previously attached to photo-chlorination.

The light sensitiveness of halogens and their compounds is summarized by Mott and Bedford [1] as follows: Fluorine, in its compounds, is wonderfully stable to light. Silver fluoride is not light-sensitive like the other halogen salts of silver. Sulfur fluoride does not yield to ultraviolet rays (or visible light) although the sulfur oxides and hydrides are sensitive to ultraviolet. As Sheppard points out, the great stability of calcium fluoride is associated with a remarkable transparency to ultraviolet. Chlorine responds to light chiefly in the blue, violet and ultraviolet. The absorption spectrum extends further into the ultra-

[1] J. Ind. Eng. Chem. 1916, *8*, 1029.

violet than that of bromine. In this connection it is of special interest to note that the photo-sensitiveness of silver chloride is apparently more marked in the ultraviolet than silver bromide. Bromine, in the free form, responds to light less in the ultraviolet than chlorine. On the other hand, hydrobromic acid is more easily decomposed by ultraviolet radiation than is hydrochloric acid. Iodine extends its spectrum still further towards the long wave-lengths and hydriodic acid is decomposed by ordinary blue and violet light.

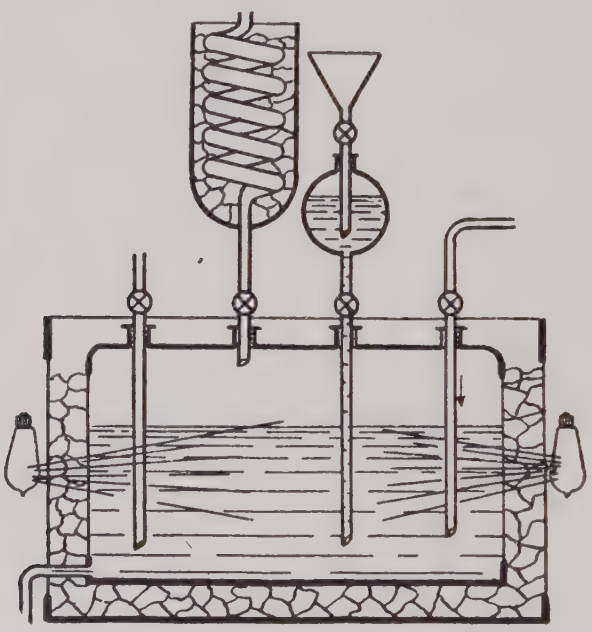


FIG. 47.—Blanc's Apparatus for the Chlorination of Aliphatic Hydrocarbons.

In the production of chlorinated compounds of saturated hydrocarbons, Blanc [2] makes use of light rays for activating the reaction. In addition to the activating effect of the light, catalyzers may also be used.

An apparatus for carrying out the process is described, see Fig. 47, in which a chamber containing the hydrocarbon to be chlorinated is fitted with windows, transparent to the light waves which are employed. In the illustration, the right-hand tube is for the admission of chlorine, the separatory funnel is for the addition of hydrocarbon; next to the separatory funnel is a reflux condenser and at the left is a tube for the return of material which has passed through the apparatus and is not sufficiently chlorinated. Ultraviolet radiation may be used, the position of the lamps being indicated by the two electrical bulbs located on the sides of the chamber. The outlet tube at the lower left-hand corner is for drawing off the chlorinated material. The hydrochloric acid given off by the reaction is absorbed, thus purifying the chlorine which is returned to the chamber; also means are described for fractionating the chlorinated

[2] U. S. Patent 1,248,065, Nov. 27, 1917.

material and returning those portions which are not sufficiently chlorinated. It is stated by Blanc that small amounts of moisture are favorable to chlorination and for this reason the chlorine is bubbled through water before entering the reaction chamber.

Brooks, Essex and Smith[3] describe a process of chlorinating liquid hydrocarbons such as gasoline, and petroleum oils, benzol, toluol, etc., in which a temperature-controlled body of such liquid hydrocarbon is treated with chlorine

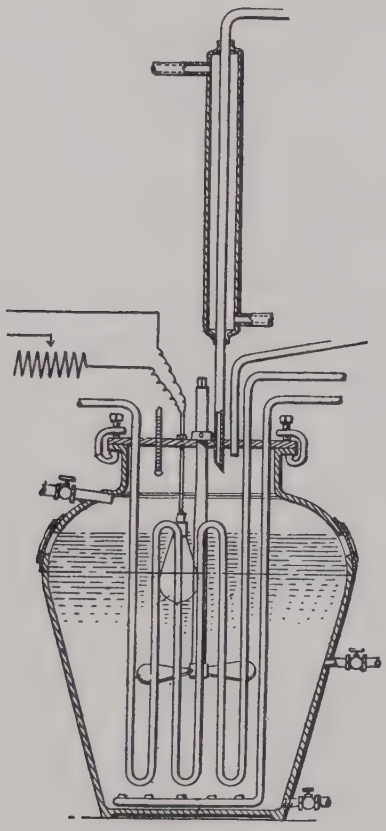


FIG. 48.

under the influence of light. The chlorine is introduced at a point in the liquid body remote from that at which the rays of actinic light enter, as by illuminating a body of liquid hydrocarbon from the top while introducing chlorine gas at the bottom. For example, gasoline, or a fraction obtained by distilling gasoline, is placed in an opaque vessel having means for controllable irradiation at one end, a mercury vapor lamp, or a nitrogen filled tungsten lamp, provided with a rheostat, being used. At the bottom of the container an inlet is provided for introducing gaseous chlorine. Means are also provided for agitating the liquid. As the rays penetrate through the liquid these cause a reaction of chlorine and the hydrocarbon. If the liquid is not circulated, the upwardly diffusing chlorine and the downwardly passing rays soon establish a zone of maximum

[3] U. S. Patent 1,191,916, July 18, 1916.

reaction somewhere between the top and the bottom. If the liquid be circulated, the action is somewhat different, since the circulation will bring a greater or less amount of chlorine-containing liquid under the influence of the rays. In so doing the concentration of the dissolved chlorine in the liquid in the irradiated zone is always small, there being a large excess of hydrocarbon over chlorine in the zone where action is taking place. This is stated to conduce to smoothness of reaction in forming monochlor derivatives. With artificial circulation the reaction is more uniform. Chlorine, dissolving in the oil, colors it yellow and as the chlorine disappears from solution by reaction with the liquid, the color of the liquid is discharged. The active rays pass through the uncolored oil, but not through the colored. Hence the less the amount of dissolved chlorine, the better the penetration of the rays. The reaction chamber is provided with a heating and cooling coil and a reflux condenser is used when the operation is carried on with heating. Means are provided for removing and collecting the hydrochloric acid formed. In making mixed butyl, pentyl and hexyl chlorides for the manufacture of artificial "amyl acetate" the chamber is filled with a liquid gasoline fraction, distilling between 25° and 45° C. and chlorine is introduced into the liquid in minute bubbles. As these pass upward they are dissolved to a greater or less extent. The liquid becomes charged with chlorine from below upward, the most concentrated solution being at the lowest point. The chlorine solution is brought upwardly toward the source of the rays by agitation. The intensity of the rays passing downwardly is diminished in proportion to the amount of chlorine in the solution and to the depth of the solution through which they pass. The amount of light therefore penetrating to the lower layers of gasoline containing greater amounts of chlorine is diminished to a degree permitting only a gentle action. See Figure 48.

The maximum action of the radiation and of the chlorine takes place in a zone in which the gasoline is in large excess and the tendency of the action of the rays is therefore merely to make the monochlor products; and not to induce further chlorination of mono compounds already produced. The chlorination is carried to a point where about 20 per cent of the material is converted into monochlorides when the operation is interrupted and the unchanged oil is separated from the chlorides by fractional distillation. If dichlorides are to be produced, the process is the same, save that in lieu of charging the container with hydrocarbons, it is charged with monochlorides. If the material to be chlorinated is not a liquid, it may be melted or dissolved, as by using carbon tetrachloride. For example, paraffin may be melted and chlorinated by this process. In the chlorination of pentane, Brooks, Smith and Essex[4] found that once the chlorinating action had started it would proceed very smoothly in diffused daylight, and that ultraviolet radiation was not necessary to effectuate the reaction. A process of Brooks and Padgett[5] involves the production of non-volatile unsaturated hydrocarbons from petroleum oils, in which the use of ultraviolet radiation is suggested. The product is stated to be suitable as a non-saponifiable substitute for linseed oil in paint compounds. For example, solar oil is chlorinated in accordance with the reaction:

$$C_{15}H_{32} + 2Cl_2 = C_{15}H_{30}Cl_2 + 2HCl$$

thereby also obtaining hydrochloric acid as a by-product. The dichloride thus obtained is then subjected to a high temperature, ranging from 350° C. to 550° C. in the presence of a catalyst when hydrochloric acid is split off with the formation of unsaturated hydrocarbon. The final product is found to have an iodine number varying from 120 to 150 according to the boiling point of the solar oil and is capable of absorbing oxygen with the formation of a "drying" film, such as is given by linseed oil.

Boyd[6] advocates a continuous two-phase system of chlorination to prepare monochlor-paraffins. Whether the chlorination of the lower-boiling members of the paraffin hydrocarbons is carried on in either the liquid or vapor phase.

[4] J. Ind. Eng. Chem. 1918, *10*, 511.
[5] U. S. Patent 1,220,821, March 27, 1917.
[6] U. S. Patent 1,293,012, Feb. 4, 1919.

the concentration of the monochlor-compounds in the liquid or vapor should not be allowed to exceed 20-30 per cent. If the concentration exceeds this percentage, the addition of more chlorine to the system leads to the formation of di- or trichlor-compounds due to the action of the chlorine on the monochlor-compounds. Consequently it is necessary that part of the saturated liquid be led to a still, where the hydrocarbon and chlorhydrocarbon are separated by distillation and at the same time unchlorinated liquid or vapors must be added to the reaction zone to replace the saturated liquid or vapor withdrawn, thus lowering the concentration so that the reaction can proceed without undue formation of di- or trichlor-compounds. In either liquid- or vapor-phase chlorination, Boyd finds there is considerable chlorine dissolved in the hydrochloric acid solution, which lowers its value commercially. The vapors carried from the reaction zone consist almost entirely of unconverted paraffin hydrocarbons, hydrochloric acid and chlorine. For instance, the condensed oil vapors carried from the reaction chamber in chlorinating pentane, showed on distillation test, 96 per cent distilling between 27°-40° C. and a chloride determination indicated less than 1 per cent. In other words the vapors carried from a liquid phase reaction zone by the hydrochloric acid gas and chlorine contain a negligible percentage of chlor-hydrocarbons. Hence Boyd first subjects the paraffin hydrocarbon in the liquid phase to the action of chlorine and reacts on the escaping vapors with chlorine in a separate chamber and in the vapor phase, leading the vapors from the vapor phase chlorination into a condenser, the condensate to a still and the uncondensed vapors to a hydrochloric acid scrubber tank, any hydrocarbon vapors from the latter going to other vapor phase chlorination units, so that the losses by volatilization are decreased to a minimum. By cutting down the volume of chlorine in the last tube all the chlorine reacts and almost none escapes to contaminate the hydrochloric acid solution.

Figure 49 shows three units of Boyd's apparatus adapted for chlorinating either liquids or vapors. Each unit is equipped with a gauge glass and with a chlorine inlet pipe in the lower part. An outlet for the chlorinated product is shown at the bottom of the lower unit. The headers of each unit are fitted with windows of quartz and are equipped with ultraviolet lamps (not shown).

An apparatus for halogenating hydrocarbons is described by Rodebush [7] in which the liquid is circulated from the main reaction vessel through a small glass tube where it is exposed to the action of the rays from a mercury vapor lamp. (See Fig. 50).

Okimaka and Sakai [8] have devised a vessel for chlorination by ultraviolet rays consisting of a closed chamber provided with a window having a lens of uviol or quartz glass, two tubes opening at the focus of the lens and another tube for exit of the product. Chlorination is conducted at the opening of the tubes under the influence of ultraviolet passing through the lens. A chlorinator in which the reacting material is irradiated and heated by passing around a source of ultraviolet rays previous to entering the main reaction vessel is also proposed by Sakai and Okimaka.[9]

Graul and Hanschke [10] produce halogenated paraffin hydrocarbons by mixing the hydrocarbon with chlorine in the dark and then exposing the mixture to ultraviolet rays.

Directions are given for making chlorhexane and heptane as follows: Normal hexane is boiled in an enameled vessel, on the water-bath, and the vapors pass

[7] U. S. Patent 1,402,318, Jan. 3, 1922.
[8] Japanese Patent 35,994, 1920; Chem. Abs. 1921, *10*, 1535.
[9] Japanese Patent 39,940, Sept. 14, 1921; Chem. Abs. 1922, *16*, 3560.
[10] U. S. Patent 1,032,822, July 16, 1912.

through a vertical fractionating column into a second vessel into which chlorine is led at the same time and in which the mixture of the components takes place. The mixture containing an excess of hexane vapor passes into a third vessel in the middle of which a mercury lamp is burning. The vapors leaving this reaction vessel are passed through a condenser in which the chlorhexane and the excess of hexane condense and pass through a siphon into the distillation

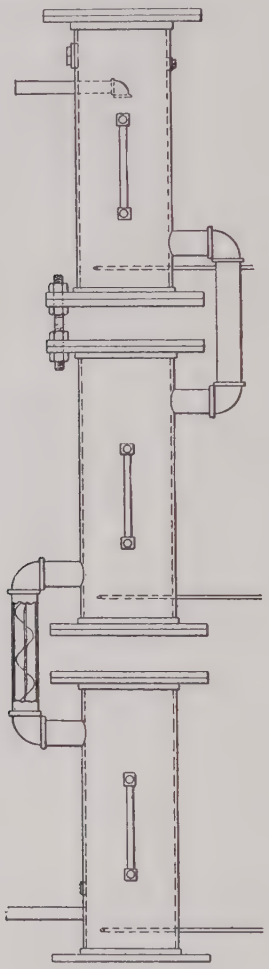


FIG. 49.

vessel, while the hydrochloric acid formed during the process is allowed to escape from the circuit. The fractionating column attached to the first vessel is maintained at such a temperature that only hexane is allowed to pass, while chlorhexane remains in the still and increases in quantity. To prepare monochlor-isoheptane, Galician petroleum having a boiling point of 88°-92° C. is purified as far as possible by repeated distillation and extraction with sulfuric acid, affording a fraction which consists chiefly of isoheptane. This is placed

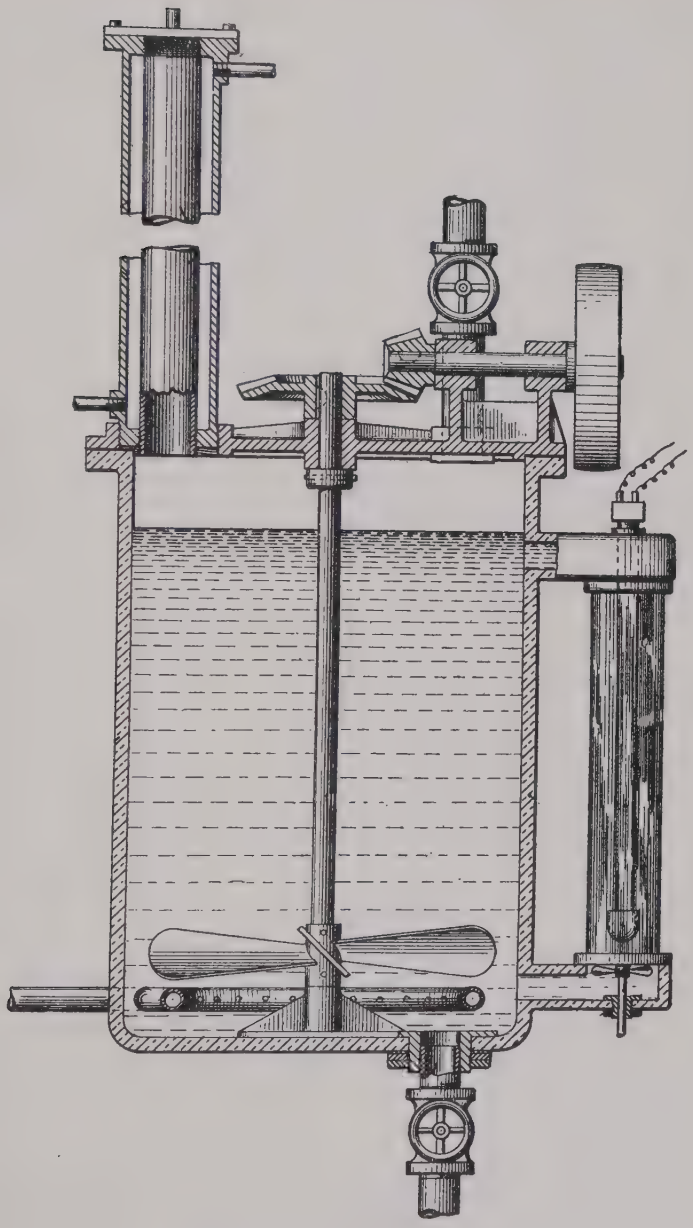


FIG. 50.—Rodebush Apparatus.

in a lead lined vessel provided with fractionating column and raised to the boiling point, at a pressure of 50 mm. of mercury. The vapors are mixed with chlorine and passed through a vessel containing a mercury lamp, whereupon chlorination takes place. In order to chlorinate 10 parts of hydrocarbon, about 7 parts of chlorine are necessary. The chlorination product consists chiefly of a monochlor-isoheptane which boils at about 140° C. and contains, according to analysis, 26.5 per cent of chlorine. By treating, in a similar manner, the repeatedly purified fraction of Galician petroleum which boils at from 75° to 81° C. a product is obtained boiling between 135° and 145° C., and containing 29.1 per cent of chlorine, while pure monochlorhexamethylene contains theoretically 29.8 per cent of chlorine. In chlorinating hydrocarbons the DuPont Company [11] have used glass tubes illuminated by a quartz lamp. Halogen derivatives of hydrocarbons, according to Pfeifer and Szarvasy [12] are produced by submitting to the action of the silent electric discharge a mixture of the hydrocarbon in the form of vapor and a halogen. The reaction may take place in presence of a catalytic agent. Eldred and Mersereau [13] state that olefins produced by cracking oil may be treated with chlorine in the presence of rays derived from a mercury vapor lamp in order to obtain chlorinated products. They note, however, that this operation requires caution since the reaction of the olefins and other unsaturated aliphatic compounds with chlorine is violent.

Baskerville and Riederer [14] investigated the action of ultraviolet on the reaction between natural gas and chlorine and reported that chlorination was not materially accelerated by ultraviolet rays, but that an acceleration was perceptible when using the rays of the visible blue spectrum.

In chlorinating methane, ethane, ethylene or similarly acting compounds Snelling [15] makes a mixture of chlorine with the material to be chlorinated which is passed back and forth between transparent baffle plates. According to Snelling [16] chlorination or dechlorination may be regulated by the action of light in a container of a glass or quartz, placed in an inverted position upon a shallow lead pan, having a lead cover. The cover or jacket has connections for the flow of steam and is also provided with openings for the supply and discharge of materials undergoing treatment. A mercury vapor lamp within the inner dome together with the regulation of temperature serves for controlling the reactions. A large excess of reducing agent assists in the dehalogenating reactions. Among various reducing agents suitable for dehalogenating, which themselves form valuable halogen derivatives in the process, are hydrogen, methane, ethane, propane, butane and carbon monoxide. The method is best adapted for use with halogen compounds which volatilize at relatively low temperatures such as the reduction of carbon tetrachloride to chloroform.

Another apparatus advocated by Snelling [17] consists of a reaction chamber, the side walls of which are impervious to light, carrying a series of parallel plates pervious to light, which are so arranged as to afford a continuous passageway for gases (chlorine and substances to be chlorinated) around the plates from the inlet at one end of the chamber to the outlet at the other. One form of the apparatus is illustrated by Figure 51.

[11] French Patent 453,406, Jan. 21, 1913.
[12] U. S. Patent 1,012,149, Dec. 19, 1911; J. S. C. I. 1912, *32*, 91.
[13] U. S. Patent 1,234,886, July 31, 1917.
[14] J. Ind. Eng. Chem. 1913, *5*, 5.
[15] U. S. Patent 1,285,823.
[16] U. S. Patent 1,325,214; Chem. Abs. 1920, *14*, 369.
[17] U. S. Patent 1,271,790, July 9, 1918.

The arrangement is such that light, directed on the apparatus, will act with greatest actinic effect on the gases nearer the outlet and with less actinic effect on the gases nearer the inlet, there being a means for regulating the temperature of the reacting gases. A Cooper-Hewitt mercury vapor lamp is recommended. With this apparatus, natural gas, methane, ethane and propane have been chlorinated. Thus Snelling has prepared carbon tetrachloride and chloroform with hydrochloric acid as a by-product. Reactions of the character described also may be carried out when the reacting materials are liquid. Even if both the reacting materials are liquid, the general method of procedure is the same, the underlying principle being in general, the bringing of the reacting materials in mixed condition past a number of semi-transparent partitions, each of which cuts off a part of the radiation so that the reacting mixtures are brought under the influence of radiation of gradually increasing intensity.

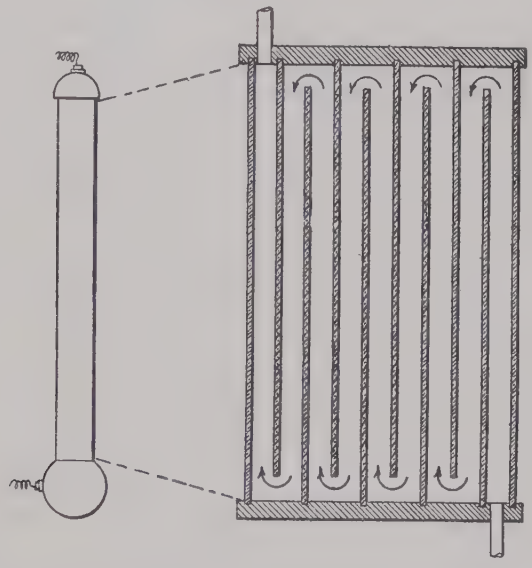


FIG. 51.—Chlorination Chamber Used By Snelling.

A different type of device for carrying out chlorination [18] consists of a dome shaped chamber of transparent material, with an inlet pipe for the gaseous reactants, and an outlet for the liquid product. A cooling coil is provided, but in order to prevent too rapid combination reliance is had upon vigorous agitation by means of fan- or propeller-shaped stirrers. Keyes [19] also describes an apparatus for the production of chlorine or bromine derivatives of hydrocarbons in which the tubular portion of a quartz mercury vapor lamp is surrounded with a jacket, having an inlet, an outlet, a vent, and a condenser. The tube may be surrounded with an inner jacket, which may be exhausted. All the parts except the electrodes, may be made of quartz. (See Fig. 52.) This apparatus is adapted to continuous operation. In operation a

[18] Snelling, U. S. Patent 1,523,563, Jan. 20, 1925.
[19] U. S. Patent 1,237,652, August 21, 1917.

mixture of halogen and hydrocarbon is fed at the inlet, and passes up and around the lamp tube, being acted upon by the radiations produced by the current and finally being delivered to the outlet. With the inner vacuum jacket around the tube, the liquids passing through the reaction jacket, are protected from the heat produced by the lamp. Sparr and Masland [20] also advocate the use of light of short wave-length for chlorination.

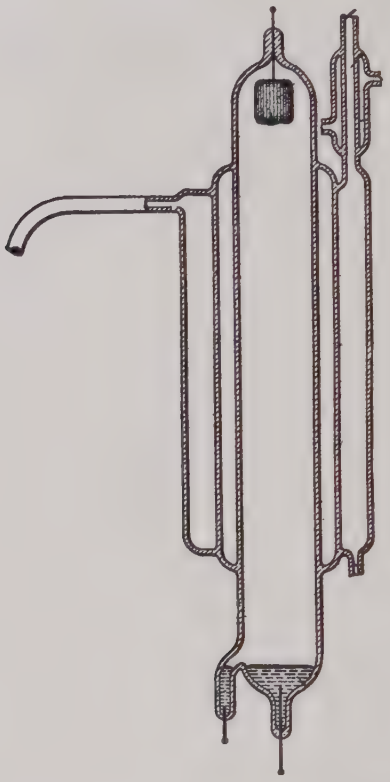


FIG. 52.—Keye's Apparatus for Chlorination.

It is claimed by Lacy [21] that if methylene chloride, water and chlorine are introduced into a closed reaction vessel and exposed to the influence of actinic light, the water forms a layer above the methylene chloride and after sufficient chlorine has been introduced to drive out the air it creates a slight pressure in the reaction vessel, and that chloroform and hydrochloric acid are produced. The apparatus described for carrying out this process is provided with a mercury vapor lamp projecting up through the bottom of the reaction vessel and ad-

[20] U. S. Patent 1,379,367, May 24, 1921.
[21] U. S. Patent 1,308,760; Chem. Abs. 1919, 2219.

justable vertically. The layer of water adjacent to the compound undergoing chlorination serves to absorb the hydrochloric acid produced.

The chlorination of natural petroleum gas under the influence of the rays of a mercury lamp has been investigated by Tolloczko.[22] The chlorination was carried out in the outer coat of an ultraviolet lamp set up in the form of a Liebig condenser. No explosions resulted, even with equal proportions of chlorine and natural gas. The temperature varied between 80° and 100°. In the chlorination with an excess of the natural gas (natural gas: chlorine = 1 : 2) the velocity of the gas stream was 4 liters per hour. A yield of 1.8 grams oily and 0.24 grams gaseous products was obtained per liter of gas. With a double passage of the gas through the chamber surrounding the ultraviolet lamp these yields increased to 1.53 grams oily and 0.38 grams gaseous products per liter. The volatile portion consisted chiefly of methyl chloride and dichlormethane. By fractional distillation the oily products were separated chiefly into dichlormethane, carbon tetrachloride, dichlorethane and tetrachlorethane. In chlorination with an excess of chlorine an oily product and solid hexachlorethane were obtained.

Bedford,[23] using the white flame arc, has made some interesting observations on the chlorination of methane.

He observes that one volume of chlorine in seven volumes of natural gas will react quickly in the presence of light from the white flame arc,[24] but without explosion. If reaction with fresh quantities of chlorine be repeated, the speed of the conversion finally slows down as the residual gas becomes diluted with chlorine, hydrogen chloride, nitrogen, air, etc., until finally no more reaction will take place without the aid of external heat. The effect of concentration of free chlorine on the chlorination of methane was studied in the following manner: Natural gas was confined in a bell jar over water at about 20° C. and chlorine was added by bubbling it in through the water. A uniform mixture of the gases was obtained by shaking the jar and splashing the water. The access of diffused daylight, during the short period, produced little or no reaction as long as the percentage of chlorine in the gases was low. Upon suddenly exposing to the white flame arc there was an instantaneous expansion of the gases, even when the chlorine content was small. After the reaction, the water was shaken up through the gases, thereby cooling them, removing the hydrogen chloride and condensing such reaction products as were liquids at the temperature of the water.

Figure 53 shows the results reported by Bedford on chlorinating natural gas, while the latter was confined over water at room temperature, the chlorine being added in increments of either 500, 250, or 125 c.c. After mixing the gases, they were exposed to the light and then cooled by shaking up with the water. After each cycle of operations, the volume of the residual gas was noted and its contraction from the original gas volume calculated. Before the experiments were started, the water was saturated with chlorine and with natural gas; the slight increase in temperature of the water, during the reaction was found to aid rather than hinder the process. Starting with three liters of natural gas there was always an unreactive residue of about 200 c.c. showing that about 2,800 c.c. would react with the chlorine under these conditions.

The horizontal dotted lines in Figure 53 represent percentages of the total contraction obtained and aid in the study of the curves.

[22] Chem. Abs. 1914, *8*, 1282; Abhandl. Krakauer Akad. Wissensch. *52*, 307; Chem. Zentr. 1913, *84*, II, 99.
[23] J. Ind. Eng. Chem. 1916, *8*, 1090.
[24] Mott and Bedford, J. Ind. Eng. Chem. 1916, *8*, 1029.

The attempt to obtain better cooling in order to prevent entirely the formation of tetrachloride, finally led to the carrying out of the reaction in the interstices between cakes of ice. It was predicted by Bedford that by filling the reaction chamber with cracked ice, he should obtain only the di- and trisubstitution products, since methyl chloride is a gas at the temperature of ice and the others should condense out before forming the tetrachloride. The first experiment in the chlorination of methane in the spaces between cracked ice presented the difficulty of improper gas circulation. After Bedford had made many variations in the apparatus, the one shown in Figure 54 solved the difficulty. An 8-liter, two neck Woulfe flask, with the bottom removed, was placed over

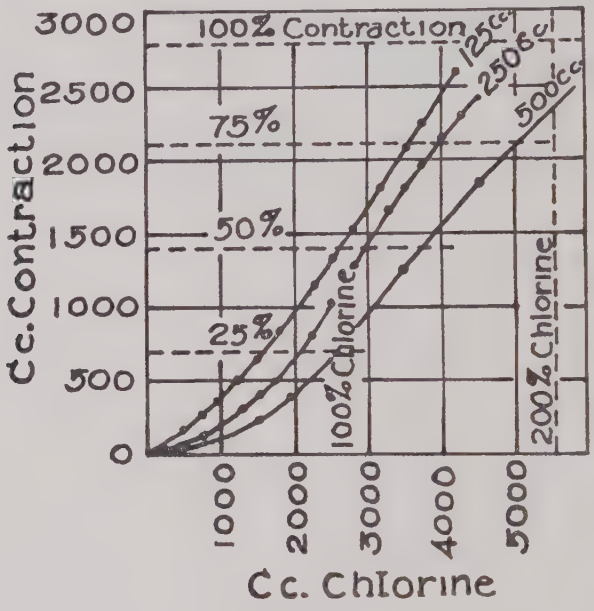


FIG. 53.

a single ice cake chipped to nearly fill the flask. As the ice melted in the top of the reaction chamber, the flask settled upon it, keeping ice in the top of the chamber where the cooling is most needed, until the bottom of the flask touched the bottom of the vat. The dotted lines show the points of highest temperature as shown by the melting of the ice. Upon starting the reaction, by means of the white flame arc-light, with the chlorine content of the gases about 1 in 8, the circulation was found to be rapid and violent. It was found that 2.6 cu. ft. of natural gas gave 166 c.c. of reaction product which is equivalent to about 17 gal. per 1,000 cu. ft. This included the methylene chloride and chloroform dissolved in the water, which were separated by distillation.

The apparatus shown in Figure 55 made of a 10-inch sewer pipe tee, was designed to prevent the access of light to the large volume of gas left in the top of the reaction chamber by the melting of the ice and also to furnish a larger supply of ice per charge. The capacity of the tile was found to be about 3¼ cu. ft. of gas per hour and a total of 18.5 cu. ft. gave 1.1 liters of product.

A large wooden reaction chamber, practically duplicating Figure 55, 28 inches by 28 inches by 44 inches inside dimensions, was built for the carrying out of the reaction on a larger scale. In one experiment using 250 cu. ft. of natural

gas, the rate of consumption varied from 14 to 30 cu. ft. per hour, and several gallons of product resulted. The analysis of the liquid reaction product separating out under water was as follows, percentages being by volume:

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
35	35	5	20

The analysis of the part soluble in the water and separated by distillation was:

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
60	28	1.5	6

About 14 per cent of the reaction product dissolves in the water produced from the melting of ice by the heat of the reaction. This soluble portion may be entirely recovered by distilling off 5 per cent to 10 per cent of the water, the

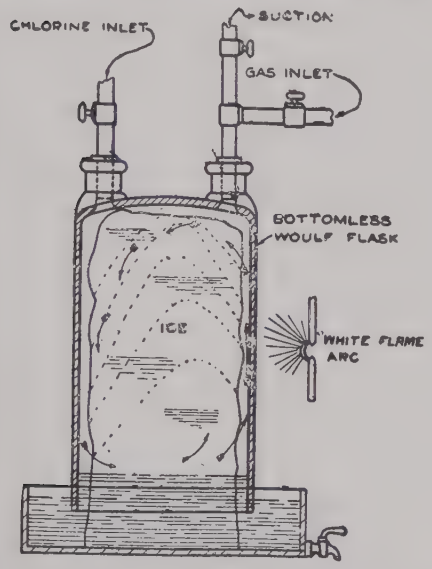


FIG. 54.—Bedford's Apparatus for the Chlorination of Methane.

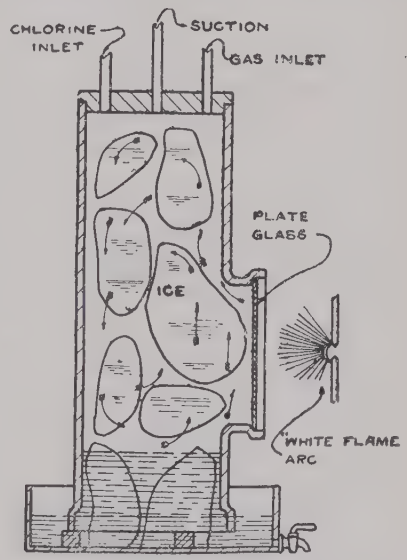


FIG. 55.—Modification of Bedford's Apparatus.

methane chlorides coming over with the distillate, and the residue being about a 5 per cent solution of hydrochloric acid, provided no water has been added except that produced by the melting of ice. About 135 lbs. of ice are necessary for the production of one gallon of product having the composition as given above and the hydrochloric acid from the reaction is thereby greatly diluted.

To ascertain the possibility of using coal gas for the production of valuable compounds, Bedford [25] subjected a mixture of chlorine and natural gas, in a chamber containing blocks of ice, to the action of light from the white flame arc and obtained a heavy liquid beneath the water produced by the melting of the ice. This liquid consisted of

[25] J. Ind. Eng. Chem. 1916, *8*, 1090.

methylene chloride, 35 per cent; chloroform, 35 per cent; carbon tetrachloride, 5 per cent and chloroethanes, 20 per cent. A portion of the product, amounting to about 14 per cent of the total, remained soluble in the water, and consisted of methylene chloride, 61 per cent; chloroform, 28 per cent; carbon tetrachloride, 1.5 per cent and chloroethanes, 6 per cent. According to the process of Tompkins [26] coal-gas, rich in ethane, is produced by distilling coal at a low temperature, e.g., 500-600° C. The ethane, together with a little ethylene, is separated by liquefaction, then again converted into gas, mixed with a suitable quantity of chlorine, and chlorinated by exposure to a quartz lamp. The hydrogen chloride produced in the reaction is absorbed in water and used to prepare a solution of a chloride, e.g., zinc chloride, from oxide or carbonate, the solution being afterward electrolyzed to produce chlorine for use in a subsequent chlorination process. The coal-gas may also be chlorinated directly, in which case the strength of the radiation must be kept below that which would cause appreciable chlorination of the methane present.

In a process for making methyl chloride proposed by Leiser and Ziffer [27] a mixture of 1 volume of methane and 6 volumes of chlorine is passed rapidly through a series of cooled reaction chambers in which it is exposed to the action of a mercury vapor lamp. To prevent the separation of carbon or the formation of products other than methyl chloride, small quantities of aqueous vapor and hydrogen chloride are added to the gases. These substances act as negative catalysts to the undesirable reactions. The product is first treated to remove by-products and the hydrogen chloride added as well as that formed; the methyl chloride produced is condensed in the usual way. The yield is high, only 15 per cent of the chlorine appearing as products other than methyl chloride. Gases containing methane may also be employed.

Payne and Montgomery [28] describe a process for making a catalyst suitable for use in chlorinating hydrocarbons. A paraffin distillate having an initial boiling point of about 450° F. (about 230° C.) or other hydrocarbon oils, such as shale oil, or such oils mixed with powdered coal, are treated in a reaction chamber at 300° F. (149° C.) with chlorine, not too rapidly at first to prevent excessive rise in temperature, until the product is a black, solid porous mass and no more hydrogen chloride is evolved. This product is a suitable catalyst for the chlorination of gaseous hydrocarbons, and if desired can be employed in the chamber in which it is formed by passing into that chamber chlorine and a moist hydrocarbon gas, e.g., natural gas or a pressure-still gas, in the proportions of about three to one by volume, to obtain the best yield of liquid chlorination products. The temperature of the reaction chamber in kept at 300° F. (150° C.). In order to complete chlorination the products are passed through quartz tubes, in which they are exposed to the rays of a mercury vapor lamp. The liquid products are then condensed, and the gaseous products, in which

[26] British Patent 780, Jan. 18, 1915; J. S. C. I. 1915, *34*, 1225.
[27] U. S. Patent 1,459,777, June 26, 1923.
[28] U. S. Patent 1,453,766, May 1, 1923.

little chlorine remains, cooled to separate methyl chloride. The liquid products are refined by treatment with caustic soda to remove hydrochloric acid and traces of chlorine, and are steam distilled. They form a transparent liquid, boiling point 134-380° F. (57-193° C.).

Gault and Truffault [29] have found that chlorine is without action on chloroform in the dark or when exposed to light of wave-length longer than 639 μμ (6390 Å). Violet light of wave-length 400 μμ (4000 Å) has a slight effect and ultraviolet rays of wave-length 300-340 μμ (3000-3400 Å) has a great effect. The reaction begins at — 5° C. and becomes rapid at 5° to 10° C. Dry chlorides of calcium, zinc or aluminum act in some degree as catalysts but ferric chloride appears totally to inhibit the reaction. This is due to its absorption of the radiations of effective wave-length, as no chlorinating action occurs when a screen of ferric chloride solution is interposed. Even in the absence of any stimulus other than ultraviolet, the reaction is complete and carbon tetrachloride results.

While studying the photochlorination of aliphatic compounds dissolved in carbon tetrachloride, Benrath and Hertel [30] found that the amount of chlorine dissolved in technical or in purified carbon tetrachloride continuously diminishes when the solution is subjected to the action of light.

If, however, the carbon tetrachloride has been previously subjected at its boiling point to the prolonged action of chlorine and then purified by treatment with nitric acid followed by sodium carbonate and chlorine again dissolved in it, the chlorine titre no longer diminishes but increases when the solution is subjected to light. Perfectly purified and dried carbon tetrachloride was shown to contain free chlorine after several days' exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a medium in which to study the photochlorination of various aliphatic compounds. The chlorine solutions employed contained about 0.05 gm. of chlorine in 10 gm. of solution. In some of the compounds investigated, one atom of hydrogen was displaced, in others two. The reaction was generally preceded by an induction period. The amount of chlorination, in some cases, was proportional to the time and in others to the logarithm of the time. If two atoms of hydrogen are displaced, the reaction takes place in distinct steps. The second displacement frequently takes place with a rapidity much greater than that at the end of the first, and is preceded by a new induction period. Chloroform, after an induction period of about 30 minutes, absorbs about 70 per cent of the chlorine required for its conversion into carbon tetrachloride. The reaction is not reversible. Tetrachloroethane was not attacked by chlorine in 3 hours. Acetic acid was converted into monochloracetic acid with very little tendency for the reaction to proceed further. Acetyl chloride and isobutyric acid behave similarly to acetic acid. With propionic acid and ethyl malonate the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen was displaced. The second atom reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were displaced in the case of n-butyric acid, both at the logarithmic rate, the two steps of the reaction being markedly distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom, then, after a slowing up, a second atom was displaced at the logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rate was neither linear nor according to the logarithmic law.

[29] Compt. rend. 1924, *179*, 467; Chem. Abs. 1925, *19*, 35.
[30] Z. Wiss. Phot. 1924, *23*, 30.

The action of chlorine on paraffins and substances prepared from the chlorine derivatives is described by Aschan.[31] The chief products investigated were the pentanes, hexanes, and a product boiling at 10 to 12° C. It was found that all the isopentyl chlorides give up hydrochloric acid under suitable conditions yielding methyl butylene which in turn unites with chlorine to form the dichloride, which by the action of bases is converted into isoprene. The dichlorisopentane obtained by direct chlorination also loses hydrochloric acid at sufficiently high temperatures and yields isoprene. Moist chlorination of isopentane gives small quantities of secondary isoamyl chloride, large amounts of primary active isoamyl chloride, and no tertiary derivatives. Pentane is less readily acted upon than isopentane. Attempts to prepare the corresponding glycol by the permanganate oxidation of methyl butylene were unsuccessful. All hydrocarbons which have at least one true ethylenic linkage can be condensed with isoprene by means of aluminum chloride to yield similar condensation products. A product termed "semi-caoutchouc" was derived by condensing isoprene with sodium, which was capable of being vulcanized.

Some of the results obtained by Benrath and Hertel on the photochlorination of aliphatic compounds in carbon tetrachloride indicate a tendency for periodicity in the photochlorination, an effect which would undoubtedly be more pronounced if longer times of exposure were employed. The results, however, are of little value, according to Plotnikov,[32] since monochromatic light was not used, and the source of light was not specified.

Volmar [33] claims that methyl sulfate readily undergoes chlorination at the ordinary temperature under the influence of ultraviolet rays, and more slowly under the influence of the light from an arc lamp or a metal filament lamp, the product in all cases being methyl chloromethyl sulfate. The fixation of a second chlorine atom is not possible because it requires radiations of such a wave-length that the dichloromethyl sulfate is decomposed as it is formed.

In the process of chlorinating methyl chloroformates as described by Kling, Florentin, Lassieur and Schmutz [34] methyl chloroformate is first prepared by the action of carbonyl chloride on methyl alcohol at as low a temperature as possible, a small amount of dimethyl carbonate being formed as by-product. By moderate chlorination in the presence of sunlight, arc-light, or the light of an incandescent lamp, the monochlor ester is obtained almost free from the dichlor which has almost the same boiling point and is therefore very difficult to remove. Further chlorination gives the dichlor ester which is easily fractionated from the small amount of trichlor ester formed. Chlorination to the limit gives the trichlor ester. Methyl formate may also be used as starting material, giving practically the same product. Grignard, Rivat and Urbain [35] claim that light exerts a marked influence on the chlorination of methyl chloroformate. In diffused light it is only the chloro-

[31] Ofvers, Finska Vet. Soc. 1915, *58*, 122; Chem. Abs. 1920, *14*, 3654. In vapor-phase chlorination of cracked kerosene better yields are obtained in diffused light than in ultraviolet according to Ragaz, Paillard and Briner, Helv. Chim. Acta 1925, *8*, 225; Chem. Abs. 1925, *19*, 2124.

[32] Z. wiss. Phot. 1924, *23*, 79.

[33] Bull. Soc. Chim. 1920 (IV), *27*, 681; J. Chem. Soc. 1920, *118*, *i*, 661; Chem. Abs. 1920, *14*, 3406.

[34] Compt. rend. 1919, *169*, 1046; Chem. Abs. 1920, *14*, 738.

[35] Compt. rend. 1919, *169*, 1074 and 1143; J. Chem. Soc. 1920, *118*, *i*, 138.

methyl ester which is formed, bright sunlight being necessary for the formation of the di- or tri- chloromethyl ester, while in ultraviolet rays the trichlor ester is easily obtained. The effect of temperature is such that up to 110-112° C. the chlorination proceeds smoothly, but at 113-114° C. it slackens very noticeably and at 117° C. decomposition begins to take place with the formation of carbonyl chloride. Catalysts, such as ferric chloride, antimony chloride, etc., are beneficial at first in the formation of the dichloromethyl ester, but when a certain concentration is reached decomposition commences, and may continue indefinitely, as some of the perchloride becomes dissolved in the liquid and continues its action.

Commenting on the manufacture of lethal gases in Germany, Carr [36] states that the preparation of diphosgene proved very troublesome. Methyl formate was chlorinated in vessels furnished with chlorine pipes and carefully lined first with lead and then with two layers of tiles.[37] These precautions are necessary, because any metal introduced into the mixture from the reaction vessel acts as an anti-catalyst. The temperature has to be carefully controlled during the reaction to obtain the best results, and further, the action of light is necessary, this being supplied by Osram lamps of 4000 candle power. The reaction takes from 6 to 8 days for completion.

Trichlorhydrin is obtained by further chlorination in the presence of a sulfur compound such as sulfur dioxide, sulfur chlorides or sulfuryl chloride, of propylene chloride or a similar compound obtained by saturating an unsaturated hydrocarbon with chlorine.[38] The sulfur compound should not exceed 1 per cent of the amount of chlorine. Sulfur dioxide and chlorine may either be introduced separately into the chlorination chamber or previously mixed, and the reaction is affected in direct sunlight or ultraviolet rays, or the light of a flaming arc, at atmospheric or higher temperatures. The product is separated by distillation from any unchanged propylene chloride.

The effect of ultraviolet radiation on the chlorination of acetic acid has been investigated by Custis.[39] Glacial acetic acid was placed in a quartz flask fitted with a reflux condenser and heated on a steam bath. Chlorine was passed into the flask and subjected to the influence of the rays from an iron arc at a distance of 3 centimeters, giving monochloracetic acid. The use of red phosphorus as a catalyzer improved the yield. If, however, the flask was placed under the influence of rays from an ordinary projection lantern at about 5 centimeters, the other conditions being the same, no chloracetic acid was obtained. No results were obtained by passing the chlorine gas through a quartz tube which was irradiated with ultraviolet before being passed into a non-irradiated flask containing glacial acetic acid.

[36] J. Soc. Chem. Ind. 1919, *38*, 468 R.

[37] The cement was said to consist of powdered fire-clay, asbestos and sodium silicate.

[38] Glysyn Corporation, British Patent 168,676, Feb. 18, 1921; Chem. Abs. 1923, *17*, 771.

[39] J. Frank. Inst. 1917, *184*, 874.

A process for the manufacture of side-chain chlorinated toluol, advocated by Gibbs and Geiger,[40] calls for ultraviolet radiation.

They note that among the various methods for the chlorination of toluol in the side chain are the following: By passing chlorine into boiling toluol in the presence of light until a certain weight of the chlorine is absorbed, a mixture of the different chlorine compounds is produced. The principal products are those in which the chlorine is substituted in the side chain, but there are also present compounds containing chlorine in the ring. On mixing toluol vapor in excess and chlorine gas in the presence of light and a catalyst, only a portion of the toluol is attacked with the production of benzyl chloride. The latter is mixed with unattacked toluol and the catalyst and must be subjected to a purification process which adds to the expense of the process. By mixing toluol vapor with an excess of chlorine gas in the presence of a catalyst a mixture of benzyl chloride, benzal chloride, benzotrichloride, chlor-toluol, chlor-benzyl chloride, etc., is produced. Gibbs and Geiger claim that when toluol in the vapor form is mixed with chlorine gas in the definite theoretical proportions to produce chlorinated side chain products and the mixture exposed to ultraviolet rays, the bodies desired are produced in greatly increased yields and without the production of interfering by-products. The operation is rendered continuous by constantly feeding to the zone of radiation the vapors of toluol and chlorine gas and by carefully regulating the speed at which these reacting substances enter the reaction chamber a high degree of purity results. They state it is advisable to work without the presence of a catalyst, as it is not essential to the reaction and would tend to contaminate the product. According to this process benzyl chloride, benzal chloride and benzotrichloride may be produced according to the proportion of chlorine employed.

According to Ransford[41] tetrachlorotoluene is obtained by passing dry chlorine into toluene in the presence of iron or anhydrous iron chloride at 12° to 15° C., the mixture being agitated. When trichlorotoluene crystallizes out, the mass is melted by heating to 45-50° C., then cooled to 35° C., and chlorine again introduced, gradually increasing the temperature to 50° C. until the necessary increase in weight has occurred. Only traces of pentachlorotoluene should be shown by precipitation on dilution of a sample with an equal volume of carbon bisulfide. On fractional distillation a yield of 90 per cent of the theoretical quantity of tetrachlorotoluene is obtained. Further chlorination at 100-130° C. in presence of light, particularly ultraviolet rays, gives tetrachlorbenzal chloride. Custis[42] has investigated the effect of ultraviolet rays (iron arc) on the chlorination of benzene and toluene. At room temperature no substitution products were obtained under the influence of the rays from an ordinary projection lantern but when exposed to ultraviolet rays chlorinated products were obtained. Toluene was chlorinated under similar conditions by passing chlorine which had been activated by ultraviolet rays before being passed into a non-illuminated flask of toluene. Benzene could not be chlorinated in this manner. Luther and Goldberg[43] have found that the frequently irregular course of the chlorination of benzene under the action of

[40] U. S. Patent 1,246,739, Nov. 13, 1917; Canadian Patent 186,466, Sept. 10, 1918.
[41] British Patent 16,317, July 8, 1914; J. S. C. I. 1915, 1203.
[42] J. Frank. Inst. 1917, *184*, 875.
[43] Zeit. physikal. Chem. 1906, *56*, 43; J. Chem. Soc. 1906, *90, ii*, 641.

light is due to the retarding effect of small quantities of oxygen. Toluene xylene, and acetic acid are affected similarly.

In the senior author's laboratory, a number of experiments have been made to compare the production of benzyl chloride, benzal chloride and benzotrichloride by the chlorination of toluol under various conditions. The best results were obtained by passing an excess of toluol vapors mixed with chlorine through a transparent quartz tube while exposing to the action of the ultraviolet radiation. The product was withdrawn from the reaction tube and the contents were collected and fractionated, the unused toluol being returned through the reaction tube. In order to determine the effect of the ultraviolet rays on this reaction the source of the rays was removed and the experiment carried out in the same manner as described above. The results of one test are given in the accompanying table.

Fraction	Quartz Tube without Ultraviolet	Quartz Tube with Ultraviolet
A. Up to 150° C.	72 per cent	42 per cent
B. 150°-170° C.	4.2 per cent	2 per cent
C. 170°-185° C.	18.5 per cent	47.5 per cent
D. 185°-215° C.	3.8 per cent	6.5 per cent

Selden Company and Gibbs [44] chlorinate benzene homologues in the side chain by passing a mixture of the hydrocarbon vapor and chlorine through a chamber exposed to ultraviolet rays. When a low-pressure mercury vapor lamp is used, a mixture of benzyl chloride and benzal chloride is produced from toluene, while a high-pressure mercury vapor lamp gives benzotrichloride. Ellis [45] describes a process for the manufacture of benzyl chloride from toluene by the continuous circulation of toluene through an apparatus in which an excess of toluene vapor is produced and acted upon by chlorine at an elevated temperature to promote side chain chlorination, under gradually increasing temperature conditions and in the presence of light to promote the chlorination. See Figure 56.

The benzyl chloride is then condensed and removed and the remaining vaporous material subsequently condensed and the hydrochloric acid substantially eliminated before the remaining toluene is returned to the still for treatment. The chlorine may be preheated before coming into contact with the toluene vapor. The treating chamber may be heated by an air heater or heating jacket. Mercury vapor lamps are arranged around the treating chamber adjacent to its discharge end. Quartz glass is used to permit the full effect of the rays to be exerted. Catalyzing material may be added to the toluene, phosphorus pentachloride being used to advantage. The preliminary portions of the chamber may also be filled with fragments of pumice, porcelain, etc., these materials considerably promoting the reaction. The treated vapors leaving the chamber contain benzyl chloride, hydrochloric acid gas, and unchanged toluene vapor. The toluene is converted to the extent of a quarter or a half during each passage. These mixed vapors are passed through a dephlegmator to collect the benzyl chloride. The remaining vapor passes from the dephlegmator into a condenser where the toluene is condensed and flows back into the still. The hydrochloric acid gas is eliminated by a separating chamber from which the gas is allowed to discharge. Additional toluene is continuously supplied to the system. Ellis

[44] British Patent 123,341, Oct. 22, 1917; Chem. Abs. 1919, *13*, 1478; J. S. C. I. 1919, *38*, 268 A.
[45] U. S. Patent 1,202,040, Oct. 24, 1916.

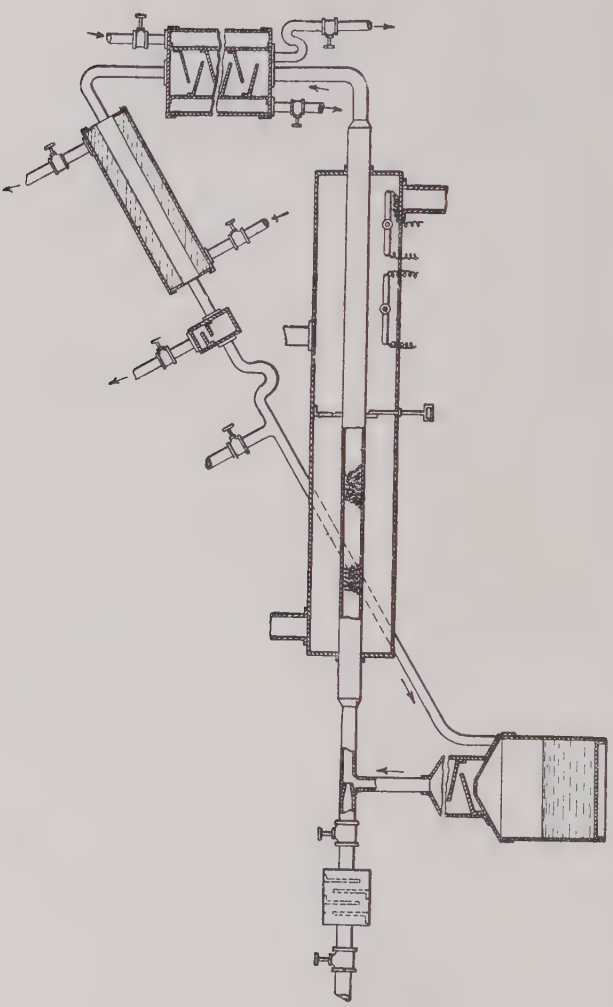


FIG. 56.

has also described[46] a special form of chamber for chlorinating toluene through the agency of ultraviolet rays. Side chain chlorination is effected, producing benzyl chloride, benzal chloride and benzotrichloride.

According to Gook and Eggert,[47] toluene, chlorinated by a stream of chlorine at 105-110°, yields a product consisting almost entirely of benzyl chloride, irrespective of whether the reaction is carried out under the influence of light or in darkness, provided a chlorine "carrier," e.g., ferric chloride, be not present. In the presence of such a "carrier," however, considerable amounts of ortho- and para-chlorotoluenes are produced. The reaction between toluene and chlorine in the absence of a carrier is practically suppressed if the temperature is reduced to —80°, and the mixture is effected in darkness. At this temperature, a photochemical reaction between these substances may be stimulated under the incidence and absorption of radiation comprising the orange and light green mercury lines. The initial reaction occurring under these conditions probably comprises the formation of hydrogen chloride together with chlorotoluene or benzyl chloride. This reaction apparently proceeds in discord with Einstein's photochemical law, as about twenty-five chlorine molecules appear to be activated per quantum of absorbed radiation. In general, it was observed that toluene and chlorine reacted with one another in darkness at —80° in the presence of a small amount of iodine. This reaction is not attributable to a sensitizing effect produced by the iodine on the components participating in the reaction.

The following is a comparison by Mott and Bedford[48] of a flame arc (at about 25 amperes and 45 arc volts on direct current) with a Heræus mercury quartz lamp on 220 volts (at 3½ to 4 amperes direct current). The Heræus quartz lamp using "Aron's" amalgam,[49] and operating under the favorable action of 220 volts, gave far better efficiencies than the 110 volt quartz lamp. Comparative experiments in chlorination, using the white flame arc and the 220 volt quartz lamp, gave the results shown in the following table.

		White Flame Arc		Quartz Lamp		
Liquid	Flask	Distance	Seconds	Distance	Seconds	Ratio
Benzol	Quartz	6 in.	2.0	6 in.	18.0	1 : 9
	Uviol	6 in.	1.9	6 in.	25.0	1 : 13
	Glass	6 in.	1.8	6 in.	30.0	1 : 17
Isoamyl Chloride	Quartz	6 in.	1.5	3 in.	3.2	1 : 2
	Uviol	6 in.	1.8	3 in.	5.0	1 : 3
	Glass	6 in.	2.0	3 in.	5.5	1 : 3
Isopentane	Quartz	3 in.	0.7	3 in.	1.5	1 : 2
	Uviol	3 in.	0.3	3 in.	0.6	1 : 2
	Glass	3 in.	0.4	3 in.	1.5	1 : 4

Chlorine gas was passed into the liquid to be reacted upon until a strong yellow color was obtained. The liquid was then divided into two equal parts,

[46] U. S. Patent 1,146,142, July 13, 1915.
[47] Z. Elektrochem. 1923, *29*, 521; Chem. Abs. 1924, *18*, 668.
[48] J. Ind. Eng. Chem. 1916, *8*, 1029.
[49] 60 per cent mercury, 20 per cent lead, 20 per cent bismuth, 0.5 per cent zinc, and 0.5 per cent cadmium.

the one part being placed in a cool, dark receptacle, while the other part was being exposed to one of the lamps. Immediately after the reaction was completed, the flask was emptied and rinsed and the second half of the reaction liquid exposed in the same flask to the other lamp. By this method the same concentrations of free chlorine were used in the same flask for each lamp, but not for each successive experiment. The results are comparable in horizontal lines only. Time was taken by a stop-watch at the moment when the color of free chlorine entirely disappeared.

A high concentration of free chlorine in a liquid with which it will react, requires comparatively little radiation to start the reaction and the lower the content of free chlorine, the greater is the ray energy necessary to bring about the speedy reaction of the halogen. The higher the temperature the less light is required for maintaining the reaction. In order therefore, to test better the qualities of the two lamps, the concentrations of free chlorine were always kept low, there being only sufficient halogen present to give a good yellow color to the liquid. The initial temperatures were also kept low (20° C.) and in every case the comparison was found to favor greatly the flaming arc.

A further comparison, for the purpose of showing the relative effect of the ultraviolet from the two sources, was accomplished in the following manner: Three flasks, almost identical in shape and capacity, were obtained in quartz, uviol glass and laboratory glass, passing, respectively rays as short as 185 μμ, 280 μμ and 400 μμ (1850 Å, 2800 Å, and 4000 Å). The same solution of free chlorine in benzol or isoamyl chloride was divided into three equal parts which were exposed simultaneously to the same light in the three flasks. The results, as tabulated in the following table show that the white flame arc emits some ultraviolet, but the amount is so small that very little efficiency is lost when working in glass apparatus.

EFFECT OF DIFFERENT MATERIALS OF CONTAINERS

Benzol				Amyl Chloride			
Light	Flask	Distance	Sec.	Light	Flask	Distance	Sec.
Arc	Quartz	8 in.	3.2	Arc	Quartz	8 in.	1.2
Arc	Uviol	8 in.	3.8	Arc	Uviol	8 in.	1.6
Arc	Glass	8 in.	3.9	Arc	Glass	8 in.	1.7
Quartz	Quartz	3 in.	7.4	Quartz	Quartz	3 in.	5.0
Quartz	Uviol	3 in.	10.0	Quartz	Uviol	3 in.	6.2
Quartz	Glass	3 in.	11.6	Quartz	Glass	3 in.	7.0

Mott and Bedford conclude that a large share of the actinic power of the quartz lamp lies in the ultraviolet rays which are not necessary or even desirable for chlorination purposes.

According to Olivier [50] when para-chlorbenzene sulfochloride in ethereal solution is exposed to direct sunlight or the rays of a uviol lamp, chlorine is liberated and oxidation takes place with the formation of the free sulfonic acid. When the experiment is carried out by passing dry oxygen through the ethereal solution of the sulfochloride while exposed to the rays of the lamp, the quantity of chlorine collected shows a deficit as compared with the equivalent of sulfonic acid formed, and aldehyde and hydrochloric acid are found in the aqueous liquid on treatment with water. It is probable, therefore; that some of the chlorine reacts with the ether to form chlorethyl ether, which is subsequently hydrolyzed to aldehyde. Under favorable conditions, the decomposition of the sulfochloride under the influence of light and oxygen may amount to over 40 per cent in 6 hours, and the reaction is practically inhibited in the absence of light or oxygen.

[50] Rec. Trav. Chim. Pays. Bas. 1916, *36*, 117; J. S. C. I. 1916, *35*, 1149.

The presence or absence of moisture has no appreciable influence. The photochemical decomposition of the sulfochloride is considerable in ethereal solution but only slight in chloroform solution. In benzene and carbon tetrachloride, the reaction does not take place. It is suggested that the formation of a peroxide may play a part in the reaction. Other sulfochlorides of the benzene series behave in a similar manner but to a lesser degree.

Schmitz & Co.[51] have prepared esters of phenol homologues, halogenated in the side chain by treating the esters alone or in suitable solvents (such as carbon tetrachloride) with halogen in the presence of light, especially from a source rich in ultraviolet rays.

Matthews, Bliss and Elder[52] have found that in the production of organic compounds halogen hydride is removed from halogen-containing compounds with the exception of mono and dihalogen hydrocarbons by treating them in the form of vapor with steam at a high temperature. The mixed vapors may also be treated with the silent electric discharge or subjected to the action of ultraviolet rays. The removal of halogen hydride may be accompanied by the removal of carbon dioxide, water, ammonia, etc. These subsidiary reactions may be effected or facilitated by means of catalysts or suitable reagents. For example, styrolene is prepared from β-bromohydrocinnamic acid.

The influence of ultraviolet radiation, in the presence and absence of catalysts, on the reactivity of a halogen bound to a carbon ring, has been investigated by Rosenmund, Luxat and Tiedemann.[53] The comparative inertness of a halogen in an aromatic compound is overcome in the presence of copper or its compounds at 180° C. to 220° C. At a temperature enough lower, so that the catalyzing action of the copper is only very slight, the radiation from a quartz mercury vapor lamp has a decidedly accelerating effect on the reaction:

$$ClC_6H_4COOH + KOH \longrightarrow HOC_6H_4COOH + KCl$$

in the absence of copper, and is still more active in its presence. At a lower temperature still, 104° C., the copper is inactive both alone and under radiation, though the radiation itself is still an accelerating agent, showing that the radiation acts directly upon the organic molecule, rather than upon the copper.

In experiments on the photobromination of toluene, made in an atmosphere of 96 per cent oxygen and 4 per cent nitrogen, LeBlanc and Aldrich[54] found that the yield of benzyl bromide was independent of the intensity of light and was constant throughout the entire portion of the spectrum investigated. The speed of the reaction decreases with decrease of wave-length and is practically zero for wave-lengths shorter than 300 μμ (3000 Å). Experiments on bromine in carbon tetrachloride and in hexane indicate that the increased reactivity of bromine in the light is not due to the splitting off of electrons. Swen-

[51] British Patent 3,053, Feb. 5, 1914.
[52] British Pat. 16,828, July 22, 1913.
[53] Ber. 1923, *56 B*, 1950; Chem. Abs. 1923, *17*, 3837.
[54] Zeit. Elektro-Chem. 1914, *20*, 543.

son [55] reports that the rate of absorption of bromine by toluene and xylene in the presence of alcohol, when exposed to the rays of the quartz mercury lamp at 20°, is retarded owing to its removal of the hydrogen bromide from the sphere of action, but that hydrogen bromide catalyzes the reaction very strongly in the positive sense, at the same time being itself decomposed.

When brominating hydrocarbons or effecting other reactions promoted by a mercury vapor lamp, Keyes [56] proposes that one of the reacting substances, e.g., bromine, be fed from a flask, into a quartz vessel, provided with a mercury vapor lamp, made integral with the flask and having a stirrer, a condenser and inlets and outlets. In another form of apparatus for similar use a vacuum jacket is interposed between an annular reaction chamber and a mercury lamp, to prevent deleterious heating of the reacting substances by the lamp.

As halogen compounds are frequently used as solvents in exact measurements, it may be noted that chloroform is comparatively unstable under the influence of ultraviolet radiation [57] and, further, that trichloroethylene is on occasions a somewhat fickle solvent, on account of its tendency to disengage hydrogen chloride.[58] It is well to recognize these properties before entrusting to the solvents valuable material which is easily hydrolyzed by traces of acids.

McLennan [59] carried on some experiments using a highly exhausted tube of fused quartz containing a few crystals of iodine. This was inserted axially in a Cooper-Hewitt mercury arc lamp with a lateral anode and a short extension at the positive end to which the quartz tube was sealed with wax. The iodine vapor tube was provided with a window of clear quartz toward which the collimator of a quartz spectrograph was directed. Iodine vapor can be stimulated to the emission a fluorescence spectrum excited by ultraviolet rays. The wave-lengths which can stimulate the fluorescence of iodine vapor lie between 210 μμ (2100 Å) and a lower limit, probably about 180 μμ (1800 Å). Resonance spectra cannot be obtained with iodine vapor when illuminated with rays from the mercury arc of wave-length shorter than 5460 Å. Portions of the ultraviolet fluorescence spectrum of iodine vapor were obtained with methyl iodide and mercury iodide at a temperature of 326°. Mercury iodide and potassium iodide at a temperature above 326° exhibit fluorescence spectra of their own when excited by the mercury arc.

When water charged with oxygen and containing also potassium iodide and hydrochloric acid is kept in the dark, the oxygen is gradually used up, and the course of the oxidation may be followed, according to Plotnikoff,[60] by determining at intervals the amount of iodine liberated. The course of the change is markedly accelerated when the reaction mixture is exposed to the mercury arc lamp, and it is shown that for this acceleration the blue rays are chiefly responsible. The solution of the reacting substances does not absorb the rays to

[55] Zeitsch. wiss. Photochem. 1921, *20*, 206; J. Chem. Soc. 1921, *120*, *ii*, 291.
[56] U. S. Patent 1,198,356; Chem. Abs. 1916, *10*, 2315.
[57] Kailan, Monatsh. 1917, *38*, 537; J. Chem. Soc. 1917, *112 i*, 209.
[58] Chem. Zeit. 1917, *41*, 901.
[59] Proc. Roy. Soc. London (A) 91, 23-9, 1914.
[60] Zeitsch. physikal. Chem. 1907, 58, 214; J. Chem. Soc. 1907, *92*, *ii*, 213.

any appreciable extent, and the velocity coefficient of the reaction is directly proportional to the intensity of the light. In the presence of uranium nitrate, eosin, starch, or copper sulfate the reaction is retarded, while in the presence of quinine sulfate, æsculin or chloroform, it is accelerated. Experiments by Tappeiner [61] on the action of fluorescein and its halogen substitution derivatives on potassium iodide have shown that the quantity of iodine liberated in the presence of light is almost the same in all cases. The activity must be independent, therefore, of the sensitiveness to light of the fluorescein.

Iodine derivatives of the paraffin series (excepting methane) in vapor form may be obtained by mixing the hydrocarbons in the dark with hydriodic acid and subjecting the mixture to the action of light rays of short wave-length or to the silent electric discharge. The reaction temperature may be reduced, according to the Badische Company,[62] by operating under diminished pressure. Warburg [63] prepared hydrogen iodide by passing hydrogen and iodine over platinum at 600°. Exposures were made in quartz for 600 and 900 seconds at $-52°$ and $-70°$ at which the vapor pressure is 343 to 118 millimeters of mercury, the radiation being derived from sparks between electrodes of zinc or magnesium. The action of light on iodine and on starch iodide in water has been studied by Bordier,[64] who added to one litre of water ten drops of 10 per cent alcoholic solution of iodine and to the same volume containing a little fresh starch paste were added three drops of 10 per cent iodine. Both suspensions were decolorized when exposed to light for a few hours, while similar suspensions not exposed retained their color. Yellow glass did not prevent or retard the action. Bordier suggests that the violet or ultraviolet rays remove the charges from the colloidal particles of iodine and starch iodide, and the iodine then combines with the hydrogen ion from the water to form hydriodic acid. After decolorization both suspensions showed acid reaction.

[61] Chem. Centr. 1906, i, 1793; Arch. klin. Med. *86*, 478.

[62] German Patent 266,119, Oct. 31, 1911.

[63] Ber. preuss. Akad. Wis. Berlin 1917, 300, Sci. Abs. 21 A, 341; Chem. Abs. 1918, *12*, 2490.

[64] Compt. rend. 1916, *163*, 205; Chem. Abs. 1916, *10*, 2669. Instead of the quartz windows used in the hitherto unsuccessful attempts to demonstrate the ionisation of iodine by ultraviolet light, an exposure chamber provided with a fluorite window, thus permitting the passage of rays of wave-lengths down to about 120 μμ, has been employed by West and Ludlam. The aluminium spark gap used was placed close to the window to prevent absorption by the oxygen of the air. A stream of nitrogen, which is not ionised by rays of the wave-length employed, carried iodine vapor of partial pressure 0.13 mm. at 15° C. It has thus been found that, provided the aluminium sparking terminals are kept free from oxide, ionisation takes place, both positive and negative charges being given to the electrometer in approximately equal amounts. The effect ceases when the source of radiation is removed 1 cm. in air away from the fluorite. The results show that iodine vapor is ionised by rays of wave-length between 185 and 120 μμ. The work of Smyth and Compton, and of Mohler and Foote on the ionisation potential of iodine indicates a corresponding wave-length of 123 or 131 μμ, while the spectrum of the aluminium spark in air shows strong lines between 170 and 180, weaker ones at 150 and 160, and a group of stronger lines at 130. Many of the molecules of iodine were probably in a state of fluorescence, and the ionisation potential of fluorescing iodine corresponds with a wave-length of 181 μμ. Proc. Roy. Soc. Edin., 1924-1925, *45*, 34.

Chapter 11.

Photosynthesis: The Formation of Carbohydrates and Proteins from Atmospheric Gases.

The mode of formation in the living plant of the great variety of substances on which our food supply depends is one of the most fascinating problems in the science of chemistry. It is peculiarly intriguing, as we know that the only sources from which the plant can start are carbon dioxide, which it absorbs from the air, and water and salts which it obtains from the soil. With the help of sunlight, the plant, in some hitherto unknown way, succeeds in building up from these simple inorganic materials those complex substances on which all animal life depends. As Spoehr [1] points out, so far as the composition of food material is concerned, there exists a closed cycle. Man feeds on animals, and animals on plants; the plants feed on the carbon dioxide given to the air by the animals as a result of the latter's use of food. Thus the plant reconverts the waste products of animal metabolism into food. The latter process is a form of photosynthesis. The plant absorbs through its leaves the carbon dioxide which is universally present in the atmosphere, and which is formed by the burning of coal, fuel oil, etc., and is also exhaled by animals. By means of the light from the sun the carbon dioxide thus absorbed by the leaves is changed into material such as sugar or wood, which can again be used as food for animals or as fuel.

The possibility of duplicating the plant's work by artificial means and under controllable conditions is an interesting one, and has engaged the attention of many able men. Several theories concerning the mechanism of reactions taking place in plant life have been advanced, but it is only during the past decade that considerable progress has been made.

In the matter of food production Sheppard [2] is of the opinion that co-operation rather than rivalry with the green plant is likely to be the order for many days. But on details, in specific by-products, as oils and resins, carbohydrates and alkaloids, the whole multitude of organic compounds, chemistry may well furnish photosynthetic processes more efficient than vegetation. None the less, it should more diligently inquire into the green leaf's secret. It has long been believed by explorers [3] in this field of investigation that the first process which

[1] J. Ind. Eng. Chem. 1922, *14*, 1142.
[2] Chemical Age, N. Y., 1923, *31*, 57.
[3] Baeyer, Ber. 1870, *3*, 68, was the first to suggest formaldehyde as the initial stage in photosynthesis.

takes place in the living plant cell is the production of formaldehyde from the carbon dioxide and water; and that the second stage is the conversion of this formaldehyde to simple sugars of the nature of glucose and fructose, these sugars then combining among themselves to give cane sugar, starch, and other complex carbohydrates, notably cellulose. The early difficulties found in accepting this theory—first, that no one had succeeded in making formaldehyde from carbon dioxide and water alone; and second, that no free formaldehyde is found in the living plant—seem now largely to be overcome. Sabalitschka [4] showed that certain plants, when deprived of carbon dioxide and supplied with formaldehyde, assimilate the latter and polymerize it to sugars and starch. This takes place even in the absence of light. The fact that these plants are able to restore their stock of carbohydrate, depleted by the absence of carbon dioxide, by making use of the formaldehyde, provides evidence for the hypothesis that formaldehyde is an intermediate product of the photosynthesis of carbohydrates from carbon dioxide and water.

Moore and Webster,[5] in experiments on fresh water algæ, also found that though formaldehyde and methyl alcohol are highly poisonous to the green cell, they can be used as nutrition in the absence of carbon dioxide, when fed at sufficiently high dilution. Very marked growths have been obtained with these substances as the sole source of carbon.

Previously the same investigators [6] confirmed and extended the work of Bach [7] and of Usher and Priestly,[8] obtaining formaldehyde by exposing carbon dioxide solutions, containing colloidal uranium oxide, to sunlight. Colloidal ferric hydroxide was also of value in catalyzing the reaction.

Attention is called by Spoehr [9] to the fact that plants have a more acid reaction in the morning, and that the acidity, for the most part, disappears on exposure to light. It is shown that certain plant acids, especially dibasic acids, readily undergo decomposition (but only in the presence of air) when exposed to ultraviolet rays in quartz vessels. Malic and tartaric acids lose two molecules of carbon dioxide under these conditions, and the alcohols thus formed are oxidized further to acetaldehyde and acetic acid. The latter acid also undergoes decomposition, yielding formaldehyde and formic acid. The last named acid yields carbon dioxide as final oxidation product. Acetaldehyde, under these conditions of oxidation, can give rise to oxalic acid. Under the conditions of oxidation, therefore, the ordinary plant acids can give rise to volatile oxidation products. This derivation of formaldehyde as a product of oxidation of acids in light throws some doubt on the significance of Baeyer's hypothesis, according to which

[4] Z. Angew. Chem. 1922, *35*, 684; J. S. C. I. 1923, *42*, 65 A.
[5] Proc. Roy. Soc. B. 1920, *91*, 201.
[6] Moore and Webster, Proc. Roy. Soc. B 1913, *87*, 168.
[7] Compt. rend. 1893, *116*, 1145.
[8] Proc. Roy. Soc. B. 1906, *77*, 369; 1906, *78*, 322.
[9] Biochem. Zeitsch. 1913, *57*, 95; J. Chem. Soc. 1914, *106*, *ii*, 120.

the aldehyde is a direct photochemical product of carbon dioxide. Stoermer and Ladewig [10] suggest that ester formation in plants is due to the ultraviolet rays of sunlight.

Griebel [11] has demonstrated the presence of small amounts of acetaldehyde in certain fruits. The so-called inclusion cells were found to contain acetaldehyde readily liberated from the cell by distillation with 2 per cent tartaric acid. The contents of the inclusion cell of Ceratonia siliqua, L, separated by mechanical means, gave a considerable amount of acetaldehyde on distillation with water alone, a further yield being obtained by distillation with acid. The acetaldehyde is considered to be responsible for the coagulation and consequent disappearance of the rough taste of the tannins during the process of ripening.[12]

From a study of the assimilatory quotient CO_2/O_2 Willstätter and Stoll [13] contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be 1; that is for each volume of carbon dioxide absorbed one volume of oxygen is liberated. In the formation from carbon dioxide of formaldehyde the quotient is 1.0; for glycollic acid 1.33; for formic acid 2.0; and for oxalic acid 4.0.

Results of work on the synthesis of formaldehyde and the carbohydrates are somewhat at variance, and the experimental evidence, particularly of the earlier investigators is at times contradictory. This is no doubt in a large measure due to non-uniformity in experimental conditions, as well as inexactness in defining those conditions. The latter may have arisen from a lack of appreciation of the nature of the radiations which were utilized and the profound selective effect of surrounding media in absorbing different portions of the ultraviolet spectrum.

In an investigation of the photochemical synthesis of carbohydrates from carbon dioxide and hydrogen in the absence of chlorophyll, Stoklasa and Zdobnicky [14] state that water does not act on carbon dioxide, exposed to ultraviolet rays, in the absence of potassium hydroxide; neither formaldehyde nor carbohydrate being formed in this case. If potassium hydroxide is added, however, formaldehyde, but no carbohydrate, is formed. The hydrogen must be in the "nascent" state for the reaction to take place, and ultraviolet rays must penetrate the reaction zone, otherwise formic acid results. A sugar is also formed when "nascent" hydrogen reacts with carbon dioxide in the presence of ultraviolet rays. The nature of the carbohydrate has not yet been definitely established. The osazone melts at 196-200°, and the carbohydrate is not, therefore, either β-formose or β-acrose.[15]

[10] Ber. 1914, *47*, 1804.
[11] Z. Unters. Nahr. Genussm. 1924, *48*, 218.
[12] Note also Power and Chesnut, J. Am. Chem. Soc. 1925, *47*, 1751.
[13] Ber. 1917, *50*, 1777.
[14] Biochem. Zeitsch. 1911, *30*, 433; Monatsh. 1911, *32*, 53; see also Chem. Ztg. 1911, *34*, 1391.
[15] The work of Stoklasa and Zdobnicky has been criticized by Bob, Biochem. Zeitsch. 1911, *31*, 358.

Stoklasa [16] notes that formic acid is first produced by the action of ultraviolet rays on formaldehyde in the presence of caustic potash with access of air or oxygen. The formic acid is then decomposed into carbon dioxide and water. Hexoses (yielding a phenylosazone with melting point 204-5°) were produced by the action of ultraviolet rays on carbon dioxide and caustic potash in the presence of ferrous compounds. No formaldehyde resulted from carbon dioxide (or acid potassium carbonate) and water under the influence of ultraviolet rays without the ferrous compounds. The carbohydrates produced during photosynthesis consisted of a mixture of hexoses (aldoses and ketoses) or their osazones. This synthetic sugar was not decomposed by Saccharomyces.

According to Berthelot and Gaudechon [17] a concentrated aqueous solution of formaldehyde is decomposed by the radiation from a quartz mercury lamp, even when the rays of wave-length less than 190 μμ are cut off. The products of decomposition consist of a mixture in almost equal volumes of carbon monoxide and hydrogen, together with (about 10 per cent) methane and carbon dioxide. Sunlight also slowly brings about the same decomposition. Formaldehyde cannot be synthesized from a mixture of carbon monoxide and hydrogen by the action of sunlight, even in the presence of catalysts, such as spongy platinum, although it is formed to some extent when the mixture is exposed to the ultraviolet rays from a quartz mercury lamp. In the photochemical reaction, $CO + H_2 \rightleftarrows CH_2O$, the equilibrium point is more markedly on the side of the decomposition products than it is in the case of the reactions $2H_2O \rightleftarrows 2H_2 + O_2$ and $2CO_2 \rightleftarrows 2CO + O_2$.

Pribram and Franke [17a] state that on exposure for some time in a quartz vessel of a redistilled 30 per cent solution of formaldehyde to light of short wave-length from a mercury vapor lamp, no external change can be noticed. If the resulting liquid is then distilled a white residue is left. The distillate possesses enhanced reducing properties acting rapidly on Fehling's solution in the cold. The residue when freed from formaldehyde is also strongly reducing and gives an osazone which melts at 168° C. This seems to indicate the formation of glycollic aldehyde, small quantities of which would pass into the distillate. The identification is not quite complete, however, since the melting point of the resulting p-nitrophenylosazone is rather lower than that of the corresponding derivative of glycollic aldehyde. Control experiments with formaldehyde not exposed to ultraviolet rays show no evidence of condensation. Coincidently with this [18] formic acid is produced along with a small amount of higher condensation products. The amount of acid formed is determined by the length of the exposure to the rays. Carbon dioxide and monoxide, hydrogen

[16] A general survey of the literature is given by Stoklasa, Zentr. Biochem. Biophys. *18*, 370.
[17] Compt. rend. 1912, *154*, 1803.
[17a] Ber. 1911, *44*, 1035.
[18] Monatsh. Chem. 1912, *33*, 415.

and methane are also produced in lesser degree. The oxygen necessary for the acid formation does not result from decomposition of the water present nor from ozone produced by the action of the rays upon air which may be present, since the formation is in no way hindered if air is excluded.

The photosynthesis of organic from inorganic compounds in the presence of inorganic colloids is the subject of an investigation by Moore and Webster.[19] In order to effect the photosynthesis of formaldehyde from carbon dioxide in aqueous solution various catalysts were tested. Undialyzed ferric chloride solution was more efficient than colloidal ferric oxide solution. Strongly positive results were obtained with uranic salts, and with 1 per cent solutions of beryllium chloride and dialyzed silicic acid; less marked but distinctly positive results with 1 per cent solutions of the chlorides of copper, nickel, manganese, and palladium and copper sulfate; negative results with the chlorides of zinc, cobalt, barium, potassium and aluminum, iron sulfate, sodium borate, telluric acid, sodium silicate, and undialyzed hydrochloric acid solution of silicic acid. The period of exposure to the rays from a mercury vapor arc in a quartz tube was 4 to 5 hours; the solutions were in transparent quartz tubes 7 centimeters from the source of irradiation. When ultraviolet rays act on a formaldehyde solution the latter acquires the power to reduce copper sulfate in the presence of sodium citrate and carbonate, a property not possessed by formaldehyde. This is evidence of a photo-condensation of formaldehyde to a reducing substance. The condensation does not require the presence of an inorganic activator, probably proceeds at its maximum velocity when the concentration of formaldehyde is approximately 5 per cent and is aided by a slight alkalinity produced by addition of sodium carbonate (final concentration approximately 0.5 per cent). The reaction occurred far more rapidly in quartz tubes than in glass tubes; short wave-lengths were the most powerful, and the limit was at about the shortest wave-lengths transmissible by glass. Both formaldehyde and paraformaldehyde underwent the condensation in aqueous solution. Attempts to isolate the new compound as an osazone or by condensation with aniline were unsuccessful. Solutions or emulsions of mono-, di-, and polysaccharides, glycerol, chlorophyll, egg albumin, milk, and vegetable juices yield formaldehyde on exposure to ultraviolet for 3 to 4 hours; sunlight produces the same change but requires a longer time. The more transparent the solution the more marked is the reaction, which apparently is one of successive hydrolysis. The change takes place far more slowly in glass than in quartz containers. The germicidal power of sunlight and certain other phenomena are thought to be closely related to this production of formaldehyde.

When formaldehyde solutions are exposed to the radiation from a quartz mercury lamp, according to Pollitzer,[20] they undergo partial decomposition into carbon monoxide, carbon dioxide, hydrogen and

[19] Proc. Roy. Soc. 1918, *90*, 168; Chem. Abs. 1918, *12*, 1992.
[20] Monatsh. 1913, *34*, 797.

methane, and partial polymerization to glycolaldehyde and higher products. The higher aldehydes have been observed to form carbon monoxide, hydrogen and the hydrocarbon corresponding with the radical to which the aldehyde group was previously attached. A reinvestigation of the behavior of the homologues of formaldehyde indicates that they decompose mainly according to the equation $R.CHO = RH + CO$; at the same time condensation takes place to some extent accompanied by polymerization to resinous substances. No pure condensation product could be isolated. Under the conditions of the experiments, in which moisture and atmospheric oxygen were excluded, no formation of acids or of esters could be detected so that the earlier suggestion of Pribram and Franke that the formic acid obtained in the illumination of formaldehyde solution is produced by the hydrolysis of previously formed methyl formate is hardly probable. From the behavior of crotonaldehyde, which, like benzaldehyde and cinnamaldehyde, gives practically no liberation of gas, it appears that the decomposition expressed by the above equation is characteristic of the saturated aliphatic aldehydes.[21]

Baly and Heilbron [22] find that detectable quantities of formaldehyde result when an aqueous solution of carbon dioxide is exposed to ultraviolet rays, with agitation. The local concentration of hydrogen peroxide formed in oxygenated water in ultraviolet is decreased by agitation and the tendency of oxidation of formaldehyde to formic acid thus is diminished, with the result that a positive test for formaldehyde may be obtained. This synthesis occurs also when the solution is exposed to visible light in the presence of a photocatalyst.

Baly, Heilbron and Barker [23] conclude that so far as plant life is concerned, the synthesis of carbohydrates is completed almost instantaneously without intermediate products, as such, existing in appreciable quantities for any length of time. They have performed many experiments along this line and have found that carbon dioxide in a water solution gives formaldehyde when exposed to rays which have a wave-length of 200 μμ (2000 Å), but that if rays having a wave-length 290 μμ (2900 Å) are present at the same time, the formaldehyde is immediately polymerized to reducing sugars. If on the other hand paraldehyde, sodium phenoxide and certain metallic salts are present in the carbon dioxide solution formaldehyde can be readily detected, but no reducing sugars, thus showing that the presence of these substances protects the formaldehyde from polymerization.

It has been claimed that certain inorganic salts serve as or yield catalysts for the production of formaldehyde from carbon dioxide and water,[24] but it is the opinion of Baly, Heilbron and Barker that in most instances the effect of these "catalyzers" is not true catalysis

[21] In the experiments conducted by Pollitzer, the aldehyde under examination was contained in a quartz flask. The mercury lamp was at a distance of 2 to 3 millimeters from the flask, but the temperature of the aldehyde never exceeded 50°.

[22] J. Soc. Chem. Ind. 1921, *40*, 377 R.

[23] J. Chem. Soc. 1921, *119*, 1025.

[24] See Moore and Webster, loc. cit.

but that their action is due entirely to the absorption of the light of wave-lengths which cause polymerization. There is, however, an exception to this in the cases of colloidal uranium and ferric hydroxide, which appear to act as true catalyzers, possibly due to the fact that they absorb light of a certain wave-length and give out light of another. Malachite green and methyl orange act in a manner similar to these uranium and ferric compounds. By their use formaldehyde may be synthesized from carbon dioxide and water upon exposure to ordinary sunlight even when protected by thick glass plates, while on the other hand in the absence of these catalyzers the formation of formaldehyde could not be detected, even on exposure to the rays from a mercury arc when the carbon dioxide solution was protected by a very thin glass plate. In the presence of chlorophyll or carotin, light having a wave-length even longer than 350 μμ (3500 Å) causes the synthesis to take place. Baly [25] considers that the secret of photosyntheses is to be found in the way in which the plant utilizes the energy of sunlight; the earlier investigations failing because the conditions of the reactions involved in the supply of the necessary light energy were not understood.

When certain colored basic substances are employed carbonic acid can be directly converted into formaldehyde in ordinary sunlight, and this is considered to be what takes place in the green leaves of the plant, the coloring matter known as chlorophyll acting in the same way as do the colored basic compounds in the laboratory.

Spoehr [26] repeated the work of Baly, Heilbron and Barker as well as that of earlier workers but was unable to get a positive test for formaldehyde. He concludes that in those experiments in which a direct reduction of carbon dioxide to formaldehyde by means of ultraviolet was reported, there existed certain essential conditions or factors not described in the publications or that there is some misinterpretation of experimental observations. Baly and his co-workers [27] assert that formaldehyde can be detected by the Schriver test on exposing cooled carbon dioxide solutions to ultraviolet radiation of 220 μμ for 18 to 72 hours. A calcite screen must be interposed if the distance between the lamp and solution is less than 6 inches. The yield is 1 to 2 parts in 100,000 but is increased in the presence of calcium or magnesium bicarbonate.

Baur and Büchi [28] have also repeated the experiments of Baly, Heilbron and Barker on the photosynthesis of formaldehyde from carbon dioxide in presence of a dyestuff, such as malachite green, and they conclude that the formaldehyde is formed, not from the carbon dioxide but from the dyestuff. The yield of formaldehyde is increased when the dyestuff is present as a colloidal solution of the color base in presence of barium hydroxide, even when carbon dioxide is entirely absent. Various experiments with dyestuffs in non-aqueous

[25] Chemical Age, London, 1922, *6*, 623.
[26] J. Am. Chem. Soc. 1923, *45*, 1185.
[27] Nature 1923, *112*, 323; Chem. Abs. 1923, *17*, 383.
[28] Helv. Chim. Acta. 1923, *6*, 959.

solution in presence of other colloids, and with the dyestuffs dyed on wool or silk or in the form of their resinates, failed to detect any photosensitizing action of carbon dioxide. The dyestuffs used were eosine, rhodamine, phosphine, and malachite green.

On repeating the work of Moore and Webster involving the use of colloidal uranium oxide and ferric hydroxide, Baur and Rebmann [29] were unable to detect formaldehyde, oxalic or glyoxalic acid.

In the study of photosynthesis it would seem that for any desired reaction it would be necessary to determine what wave-lengths of light are influential in causing the desired change to take place, and those which are detrimental to the reaction. After this has been done the question of finding suitable light filters, which could be placed either in the reacting solution itself or interposed between the source of light and the reaction chamber, would have to be solved. Then, by slight shifting of the wave-lengths from one side to the other, the optimum conditions could readily be found.

Another controlling factor is the hydrogen ion concentration. Baly [30] finds that little or no reducing sugars are formed if the solution is acid and the yield of these compounds is also very much reduced in the presence of alkali. The optimum condition is obtained when the free acidity is neutralized by means of precipitated magnesium carbonate. During the photosynthesis of the reducing sugars the solution becomes acid and it is necessary therefore to add magnesium carbonate from time to time, so that it is always present in excess. In practice, however, it has been found that when the reducing power of the solution reaches about 2 per cent calculated as glucose, a secondary reaction results in the deposition of magnesium carbonate on the walls of the quartz vessel on the side exposed to the radiation. Although the yield of sugars in a given time is less, it is more satisfactory to use precipitated calcium carbonate in place of the magnesium salt, since the former is not photochemically deposited at any concentration of sugars yet reached. The hydrogen ion concentration actually employed therefore is that of a saturated solution of calcium bicarbonate.

The temperature of the mixture during photosynthesis is also important, and Baly recommends 37° C. (99° F.) as the optimum temperature.

Comparatively large amounts of reducing sugars have been synthesized [31] by exposing aqueous 40 per cent formaldehyde solutions to the radiation of a quartz mercury lamp in the presence of calcium carbonate. A considerable amount of ozone is formed by the lamp, which is detrimental, because it absorbs rays of wave-length necessary for the synthesis, while, through diminution of the amount of oxygen, the very short wave-length radiations, usually absorbed by the latter are transmitted and cause decomposition of the sugars. The yield is increased by employing a blast of air to remove the ozone.

[29] Helv. Chim. Acta. 1922, *5*, 828.
[30] Ind. & Eng. Chem. 1924, *16*, 1018.
[31] Baly, loc. cit.

After a somewhat extended and involved concentration operation the sugars are obtained in the form of a viscous syrup with a marked sweet taste, and showing fluorescence. The reducing power varies from 34 to 25 per cent calculated as glucose. Pentoses and trioses are absent.

Irvine and Francis [32] have examined a syrup produced as described and conclude that: polysaccharides and anhydro sugars are absent, no ketoses are present; the syrup contains approximately 9.3 per cent sugar, and at least 80 per cent non-sugar compounds containing hydroxyl groups. The reactions of the latter suggest polyhydroxy phenols. Hydroxy acids or their lactides are also present in considerable amount.

The work of Baly and his associates attracted the attention of chemists and instigated much experimental effort. Using especially purified carbon dioxide and conductivity water, Porter and Ramsperger [33] were unable to duplicate the results of Baly.

In one experiment 18 liters of carbon dioxide saturated with water vapor was forced through a quartz tube 15 cm. from a 220-volt mercury vapor lamp during an interval of 60 hours. The gas, after passing the lamp, was bubbled through 15 c.c. of distilled water. In another experiment 300 c.c. of carbon dioxide, saturated with water vapor and in contact with 300 c.c. of water in a sealed container, was passed back and forth under the mercury vapor lamp at the rate of 10 c.c. per minute for 45 hours. In a third experiment an aqueous solution of carbon dioxide in a sealed quartz tube was exposed for 36 hours, but no formaldehyde nor reducing sugar was produced in any of these experiments.

These investigators believe that if formaldehyde is formed from carbon dioxide and water alone, under the influence of ultraviolet radiation, the reaction is reversible and the ordinary mercury vapor arc provides the energy required to decompose formaldehyde as fast as it is formed. The question must be settled by determining whether or not there is a definite region in the ultraviolet spectrum that will invariably supply the energy required for the reduction of carbon dioxide and which lacks the power to bring about the polymerization or decomposition of formaldehyde. It has also been suggested that impurities normally present in the reagents may be of importance in enabling the reaction to proceed, acting perhaps as carriers for the oxygen produced.

Dhar [34] has been able to synthesize, in glass vessels exposed to tropical sunlight, several organic and inorganic compounds which have been obtained by Baly and his co-workers,[35] using quartz vessels exposed to ultraviolet from a mercury lamp, and is of the opinion that ordinary chemical reactions may be sensitive to several radiations, the effects of which are additive.

[32] Ind. & Eng. Chem. 1924, *16*, 1019.
[33] J. Am. Chem. Soc. 1925, *47*, 79.
[34] J. Chem. Soc. 1923, *123, 124*, 1860.
[35] Loc. cit.

Kogel [36] is of the opinio nthat inositol and hexaldehyde in the plant are formed by photosynthesis according to the following scheme:

Tetrahydroxyethylene ⟶
hydrate of hexaketohexamethylene ⟶ inositol.
Inositol ⟶ cyclohexanone ⟶ hexaldehyde.

Tetrahydroxyethylene is considered to be an intermediate product in the formation of formaldehyde from carbon dioxide. Keto-enol changes also probably play an important rôle in the photosynthesis of formaldehyde and sugar. Guillemin [37] states that the short waves are very effective in the reduction of carbon dioxide and the fixation of carbon. As leaves age their photosynthetic activity is reduced, insufficient carbohydrate is formed for respiration, and the proteins furnish the carbon chains for this purpose. This is accompanied by a decomposition of chlorophyll, and as the yellow pigments remain constant in amount, the leaves become yellow. Meyer [38] considers the chloroplast the storage organ for proteins produced in the leaf, and is perhaps the seat of protein synthesis. The effect of ultraviolet rays in the sugar cane, pineapple and banana industries has been investigated by Tsuji.[39] By the aid of ultraviolet he noted a stimulation in the growth of sugar cane and an increase in the percentage of sugar. According to Maquenne and Demoussy [40] ultraviolet rays when applied in the proper manner are very beneficial to the growth of flowers and other vegetation. (See Chapter 13.)

Reinhard [41] observed that the leaves of beans, peas and white acacia produce starch when immersed in a 10 per cent sugar solution, and exposed to light.

Certain plants have been found by Sabalitschka and Riesenberg [42] to assimilate formaldehyde in the dark with the formation of sugar and starch.

There can be little doubt that the photosynthesis of carbohydrates in the living plant is a photocatalytic one,[43] chlorophyll or carotin probably being the photocatalyst, absorbing light of wave-length longer than 350 μμ (3500 Å) and perhaps radiating it at infra-red frequencies which are re-absorbed. That the development of some internal factor other than chlorophyll is required is indicated by the observations of Dixon and Poole, given below.

In experiments to show the significance of the action of ultraviolet rays on the photochemical synthesis of carbohydrates in cells containing chlorophyll, Stoklasa [44] observed that after irradiation the young leaves of etiolated seedling of Pismu, Zea mais, Avena and

[36] Biochem. Zeitsch. 1919, *95*, 313; 1919, *97*, 21.
[37] Compt. rend. 1857, *45*, 62.
[38] Flora, 1918, 11, 85; Chem. Abs. 1920, *14*, 2010.
[39] Louisiana Planter 1918, *60*, 413; Chem. Abs. 1918, *12*, 1842.
[40] Compt. rend. 1909, *149*, 756.
[41] Compt. rend. Soc. Biol. 1923, *89*, 1274.
[42] Biochem. Z. 1924, *144*, 545.
[43] Baly, Heilbron and Barker, J. Chem. Soc. 1921, *114*, 1031.
[44] Strahlentherapie 1915, *6*, 119; Zentr. Biochem. Biophys. 1915, *18*, 370.

Hordeum showed a dark green coloration in 2 hours, while solar radiation caused a similar color only after 6 hours' exposure. Longer exposure did not injure the cell plasma. The cells of flowers, as well as those of plants grown under glass, were, however, more sensitive toward ultraviolet rays than the cells of green leaves. Crude chlorophyll in alcoholic solution was not decomposed by the action of ultraviolet rays during an exposure period of 5-60 minutes. Alcoholic solutions of chlorophyll (from spinach) in quartz vessels were exposed by Bierry and des Bancels [45] to the light of two mercury vapor lamps for 24 to 48 hours. The solutions became faintly yellow and no longer showed the absorption bands characteristic of chlorophyll. Tests for urobilinogen were applied, with positive results. A benzene solution of chlorophyll became colorless under the same conditions, but did not show the color reactions of urobilinogen. According to Dangeard [46] when light is allowed to act on a mixture of chlorophyll and pinaverdol, the former is first decolorized at its own absorption band. The latter is attacked and finally destroyed through the energy absorbed by the chlorophyll, and not by that absorbed itself. The experiments have been extended to a variety of colored substances, with the general result that radiations which are completely inactive towards a pure substance are found to become active in the presence of a second pigment. Since chlorophyll in the plant is accompanied by various yellow pigments, such as carotin and xanthophyll, and decolorization is complete it follows that these pigments are also attacked and ultimately decomposed through the energy absorbed by the chlorophyll.

A simple method of demonstrating the production of aldehyde by chlorophyll and by aniline dyes in the presence of sunlight is described by Osterhout [47] which consists in extracting chlorophyll from fresh leaves by means of alcohol, shaking the alcohol with carbon tetrachloride and sprinkling the latter on filter paper in amounts sufficient to give it a deep green color. The treated paper is placed in air-tight bell jars with a large Petri dish containing 5 cubic centimeters of water. Some of the sheets are kept in the dark, and others in the light until the chlorophyll is bleached to a pale green, which may require several days. The water in the dishes kept in the dark gives negative tests for aldehyde, while that in the dishes kept in the light gives positive tests. Aniline dyes substituted for chlorophyll also give a positive indication for aldehydes.

Electrical measurements made with metallic plates coated with chlorophyll in different ways and illuminated from different sources of light indicate, according to Dixon and Poole,[48] that those wavelengths of light which are effective in photosynthesis are unable, to any appreciable extent, to expel electrons from the leak-pigment complex, and hence cannot in this way produce ionization or bring about re-

[45] Compt. rend. 1911, *153*, 124; J. Chem. Soc. 1911, *100*, 735.
[46] Compt. rend. 1913, *156*, 1844.
[47] Am. J. Botany 1918, *5*, 511.
[48] Sci. Proc. Roy. Dubl. Soc. 1920, *16*, 63; J. Chem. Soc. 1920, *118*, *ii*, 343.

actions external to the pigment. The action apparently occurs within the molecule of the chlorophyll itself, the atomic groups of the leaf pigment entering into the action of photosynthesis and participating in the combinations and decompositions which ultimately lead to the formation of carbohydrates and the evolution of oxygen. The developing leaf at first lacks photosynthetic power; and development of this power lags behind greening; hence photosynthesis demands the development of some internal factor other than chlorophyll. The photosynthetic potentiality of this factor increases rapidly with age, day by day, whether the leaf be in the light or in darkness, and even though no concurrent increase occurs in the amount of chlorophyll. This has been demonstrated by Briggs [49] by exposure of the leaf to illumination for photosynthesis while confined in an atmosphere of hydrogen containing merely a trace of oxygen. Under these conditions the initial amount of chlorophyll does not increase. The photosynthesis was measured in an atmosphere of hydrogen to which carbon dioxide had been added. The partial pressure of the oxygen produced was kept extremely low by its rapid removal. When a leaf is cut from a seedling of the dwarf French bean (Phaseolus vulgaris) in the dark at an early stage and is partially greened by exposure in air to the action of light, it possesses very little or no photosynthetic activity, but if the same procedure is applied to a similar leaf from the same plant a few days later, the photosynthetic activity has become quite marked.

As to the actual part which chlorophyll plays in the photosynthesis of carbohydrates in the living plant, Thatcher [50] points out that three possible modes of action are now receiving experimental study. The first of these, which has naturally been longest considered as the probable function of chlorophyll, is that it acts chemically as a catalyst by forming unstable intermediate products with formaldehyde or possibly other simple intermediate compounds of the photosynthetic process. Indeed, several investigators [51] have shown that chlorophyll actually does form a compound with formaldehyde from which complex the formaldehyde may be either given off or absorbed in order to establish a proper equilibrium in the photosynthetic process, and to afford in the plant a mechanism by which the quantity of free formaldehyde is regulated. In this way the amount present in free form at no time reaches that which would be toxic to the cell protoplasm. The second of these conceptions is that, regardless of the color and of the general chemical reactivity of chlorophyll, the mineral constituent (magnesium) which it contains is held in proper colloidal form to exert a definite catalytic effect upon the photosynthetic process. The third, and most recent, explanation of the mechanism of chlorophyll action is that the pigment acts as a photocatalyst, or light screen, to absorb and transmit the energy from light rays of the proper wave-length to accomplish the several steps in the photosynthesis of carbohydrates.

[49] Proc. Roy. Soc. (London), 1920, *91B*, 249.
[50] J. Ind. Eng. Chem. 1922, *14*, 1146.
[51] Proc. Roy. Soc. 1908, *80 B*, 30; 1910, *82*, 226.

As has been pointed out above, this last conception, at least in its broader aspects, has very recently been given some measure of experimental confirmation, and the artificial synthesis of simple carbohydrates from atmospheric gases under the influence of proper photocatalysts has already been accomplished.

From theoretical considerations Heilbron [52] thinks it is improbable that the chlorophyll complex alone could absorb sufficient energy to complete the process.[53] If the reaction takes place in stages and both of the chlorophyll pigments and the two carotinoid pigments are involved sufficient energy can be accounted for theoretically. Spectrographic evidence obtained from a study of pure carotin indicates that carotin is transformed into xanthophyll. Each pigment could function according to the following scheme: Chlorophyll "a" carbonic acid $\longrightarrow$ chlorophyll "b" hydrate + HCHO. Chlorophyll "b" + carotin = chlorophyll "a" + xanthophyll.

Other theories concerning the function of chlorophyll have been advanced and it is highly probable that this substance may play more than one rôle in the physiology of the plant. It is, however, beyond the scope of this work to enter into a detailed discussion of the chemistry of chlorophyll and related pigments.

Paralleling the production by plants of carbohydrates from carbon dioxide, and in a large measure complementary to that series of reactions, is the photosynthetic utilization of nitrogen, culminating in the formation of proteins. These substances, equally with the carbohydrates, claim attention on account of their great importance as foods. According to Moore,[54] sunlight causes a slight amount of union of the nitrogen and oxygen of the air, resulting in the formation of nitrogen pentoxide and nitrogen trioxide. These oxides and the nitrates and nitrites derived therefrom are utilized by green plants as sources of nitrogen.

Moore and Webster [55] assert that though plants utilize easily available nitrogen in the form of nitrates and nitrites, they are not dependent on these, and are able to fix atmospheric nitrogen. In experiments on fresh water algæ these investigators showed that nitrogen oxides are assimilated in the presence of sunlight but only if sufficient carbon dioxide or its equivalent is furnished to nourish the plant. Many investigators, however, hold that the plant's only source of nitrogen is that absorbed through the roots, which is already in combination as nitrate or nitrite. Laurent found that plants are able to convert nitrate to nitrite, and it was observed by Thiele [56] that the radiation of a quartz mercury lamp produces the same change rapidly, with the evolution of oxygen.

The controversy as to whether plants are able to utilize atmospheric nitrogen directly, without the intermediate formation of nitrates or

[52] J. Soc. Chem. Ind. 1924, *43*, 89T.
[53] Chem. Abs. 1921, *15*, 3072.
[54] J. Chem. Soc. 1921, *119*, 1555.
[55] Proc. Roy. Soc. B 1920, *91*, 201.
[56] Ber. 1907, *40*, 4914.

nitrites, and without the intervention of bacteria, is an old one. For some time it was regarded as settled in the negative by the results obtained by Boussingault [57] and by Lawes, Gilbert and Pugh.[58] Later opinion has inclined toward the view that certain plants, at least, have the power to fix nitrogen directly. Among those whose experiments uphold this opinion are Ville,[59] Jamieson, Wann,[60] Mameli and Pollacci,[61] Moore and Webster [62] and others.

With a variety of plants belonging to a diversity of orders from the algæ to the phanerogams, Mameli and Pollaci [63] have proved that many, if not all, green plants possess the power of fixing elementary nitrogen from the air. They worked with plant cultures which were treated so as to be free from bacteria, and they supplied to the plants nitrogen which was freed from ammonia and other nitrogen compounds. They measured the amount of elementary nitrogen at the beginning and at the end of the experiment and found that fixation of nitrogen corresponded to loss of elementary nitrogen from the space in which the plants were growing.

Lipman and Taylor [64] experimented extensively with wheat, barley and peas, using precautions to insure the absence of ammonia and nitrogen oxides from the air supplied. Amounts of nitrate varying from the full amount theoretically required, to none, were supplied to the culture solutions. The results indicate that even with complete absence of nitrogen from the culture solution, wheat and barley can utilize atmospheric nitrogen, but peas cannot. *Bromus* shows a slight power to fix nitrogen.

Either diffused daylight or ultraviolet, according to Baudisch,[65] causes methyl alcohol to react with potassium nitrite with the production of the potassium salt of formhydroxamic acid, CHOH :NOK.[66]

Baly, Heilbron and Hudson [67] report that activated formaldehyde, such as is photosynthetically produced from carbon dioxide and water under the influence of ultraviolet rays or visible light in presence of a photo-catalyst, reacts rapidly with nitrites with the formation of formhydroxamic acid, the reaction taking precedence to the polymerization of the formaldehyde to reducing sugars. Photochemically activated formaldehyde possibly has the constitution H·C·OH, and its union with potassium nitrite could take place as follows:

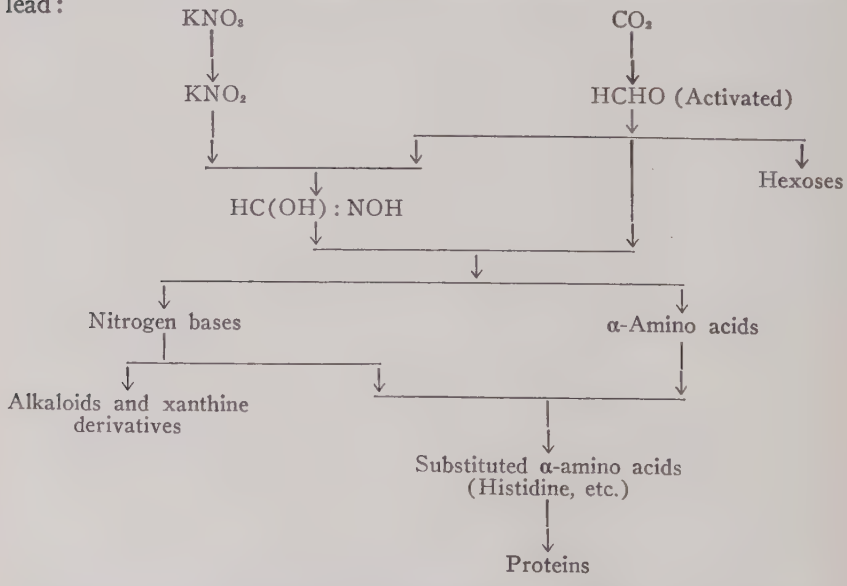
$$\mathrm{H\cdot C\cdot OH + O:N\cdot OK \longrightarrow \begin{matrix}\mathrm{H\cdot C\cdot OH}\\ \|\\ \mathrm{O\cdot N\cdot OK}\end{matrix} \longrightarrow \begin{matrix}\mathrm{H\cdot C\cdot OH}\\ \|\\ \mathrm{N\cdot OK}\end{matrix} + O.}$$

[57] Ann. de Chim. et Phys. (3), *43*, 1855; Trans. Roy. Soc. *151*, 452.
[58] Trans. Roy. Soc. *151*, 431.
[59] Trans. Roy. Soc. *151*, 455.
[60] Am. J. Bot. 1921, *8*, 1.
[61] Atti. del Ist. Bol. Univ. Pavia (II) *14*.
[62] Loc. cit.
[63] Loc. cit.
[64] J. Frank. Inst. 1924, *198*, 475.
[65] Ber. 1911, *44*, 1009; 1916, *49*, 1176; 1918, *51*, 793.
[66] See also Hepworth, Chemical Synthesis, New York, 1924, 8.
[67] J. Chem. Soc. 1922, *121*, 1078; J. S. C. I. 1922, *41*, 609 A; Chem. Abs. 1922, *16*, 3463.

Formhydroxamic acid marks the first step in synthesis of the nitrogen compounds found in the plant, and it reacts further in various ways with activated formaldehyde to give α-amino acids and nitrogen bases, these condensations taking second order of preference, all excess of activated formaldehyde polymerizing to hexoses. Thus formhydroxamic is converted into the compound CHOH : NH, with the loss of oxygen, and this compound reacts with activated formaldehyde, forming a ring compound which rearranges itself to glycine CH_2NH_2COOH. Further condensations and substitutions yield other α-amino acids. Condensation of three and four molecules of formaldehyde, with subsequent loss of water and oxygen yields pyrrole and pyridine respectively.

The photosynthesis of the nitrogenous compounds from formhydroxamic acid is extraordinarily rapid and soon goes far beyond the formation of simple compounds; the amino acids, pyrrol and pyridine derivatives condensing further to xanthine bases and substances of an alkaloidal nature. Two different alkaloids have been isolated in this way, one a volatile oil with an odor resembling tobacco, and the other a solid of low melting point and an odor of burnt feathers. Both form crystalline salts and gave positive tests with alkaloidal reagents. Positive evidence is also obtained for the formation of at least one substituted amino acid resembling histidine in its reactions. The photosynthesis of proteins would represent one stage further in the process, although positive evidence of their formation in vitro has not been obtained.

The following table shows the general scheme to which the results lead:



The results leave no doubt that the activated formaldehyde synthetically produced in living chloroplast reacts with potassium nitrite with ex-

traordinary ease to produce formhydroxamic acid which at once condenses with more of the activated formaldehyde to give various nitrogen compounds. It follows from this that the synthesis of the nitrogen compounds found in the plant is not photo-synthetic except in so far as the production of the activated formaldehyde by the chlorophyll is concerned.

Although free ammonia does not exist in the plant, and is in fact a poison for it, Baly, Heilbron and Stern [68] consider the photosynthetic reaction of ammonia and formaldehyde important. They point out that ammonium nitrate may be present, and this may react with formaldehyde to give formhydroxamic acid and ammonia. After exposing a 1.3 M solution of ammonia saturated with carbon dioxide to the rays of a quartz mercury lamp, these investigators isolated methylamine, and demonstrated the presence of nitrous and nitric acids. Pyridine was also found. Such syntheses proceed normally only under the influence of ultraviolet of short wave-length, no reaction taking place on exposure of the ammonia-carbon dioxide solutions in glass tubes behind a plate glass screen. If ammoniacal solutions of cupric carbonate saturated with carbon dioxide are exposed behind glass to the radiation from a mercury lamp, methylamine and pyridine or piperidine are formed.

When the same investigators [69] exposed 2 M solutions of formaldehyde and ammonia to ultraviolet for periods of 6 to 10 days, they obtained, in addition to the products mentioned above, a brown solid giving the reactions of alkaloids. From chemical and pharmacological tests they conclude that the alkaloid is coniine. In this and other syntheses no compounds intermediate methylamine and pyridine thus far have been detected, and it is significant that no alpha-amino acids, nor reducing sugars were formed. Attention is called to the fact that the more complex products of photosynthesis are slowly decomposed by ultraviolet rays of very short wave-length. A screen more effective than any known at present is necessary, to absorb this radiation while permitting that essential to the photosynthesis to pass.

Hepworth [70] points out that the synthesis of proteins can also take place in the dark, and in tissues free from chlorophyll, provided an adequate supply of carbohydrate is available, and considers the evidence good in favor of the view that nitrogen assimilation is not a photochemical process, light being of only indirect importance in providing a means for the formation of carbohydrates.

The evidence adduced by Baly, Heilbron and Stern [71] to show the presence of coniine, and of pyridine, in solutions of formaldehyde and ammonia exposed to ultraviolet light is considered insufficient by Snow and Stone,[72] who point out that the products of the normal interaction of ammonium chloride and formaldehyde—tetramethyl-methylenediamine and methylmethylene imine—give the same tests.

[68] J. Chem. Soc. 1923, *123*, 185; Chem. Abs. 1923, *17*, 1421.
[69] Loc. cit.
[70] Chemical Synthesis, New York, 1924, 12.
[71] Loc. cit.
[72] J. Chem. Soc. 1923, *123*, 1509; Chem. Abs. 1923, *17*, 2865.

Chapter 12.

Sterilization by Ultraviolet Rays.

It has been known for nearly half a century that the ultraviolet rays are capable of killing low organisms, such as bacteria: but it is in only comparatively recent times that this knowledge has received practical application.

The following summary gives the leading conclusions on which workers are in substantial agreement, and a consideration of it will assist the reader in following the sometimes devious ways by which these conclusions have been reached.

1. The bactericidal action is practically confined to the middle ultraviolet, i.e., to the region between wave lengths 297 μμ and 210 μμ (2970 Å and 2100 Å). The extreme limits under consideration in this chapter are 350 μμ and 185 μμ.

2. The usual photochemical laws apply: The active rays are those which are absorbed by the body acted upon; the total effect is a function of the intensity of the radiation and of the time during which it acts.

3. The action is a direct one of the rays upon the bodies of the bacteria, and is not due to the formation of germicidal substances, such as hydrogen peroxide.

4. The action is exerted, chiefly if not entirely on the protein constituents of the bodies of the organisms. Within the protein molecules, there is strong reason to believe that it is the aromatic amino-acids that are specifically attacked.

5. The penetration of the rays into organic matter is extremely feeble: They are, for example, arrested by the thinnest layer of skin. As a corollary of this, turbidity of a liquid greatly obstructs the sterilizing action, while color is not of so much importance.

6. Free oxygen is not necessary to the action.

Early History.

We will now consider, in outline, the history of the investigation and of the application of the sterilizing power of ultraviolet rays.

As early as 1877 Downes and Blunt discovered the bactericidal action of light.[1] Working with such casual mixtures of organisms as are met with in putrefying substances they established:

1. That the bactericidal action was due to the rays of short wavelength, including the ultraviolet.

[1] Downes and Blunt, Proc. Roy. Soc. 1877, *26*, 488.

2. That dried matter was at least as easily sterilized by the rays as was moist matter.

They were of opinion that the action was exerted directly on the organisms and that it was not due to changes produced in the medium.

They thought that they had established the necessity for the presence of free oxygen. In this they were, undoubtedly, in error. This error persisted for a long time, being repeated and emphasized by Roux in 1887, until it was corrected by Marshall Ward in 1892. It is instructive to consider the causes for this mistake. The early experimenters used the whole radiation of the sun, or of the arc lamp. When attempting to test whether the exclusion of oxygen would prevent the sterilizing action, they adopted one of two methods. Usually, they enclosed the test culture in an exhausted glass tube and exposed this to the rays. Now we know that glass absorbs all but the longest of the ultraviolet rays: and that although these investigators had eliminated oxygen, they had simultaneously shut out the active rays. Occasionally they caused the rays to fall normally to the surface of a culture on a solid medium. Observing that in this case only the upper layers were sterilized, they concluded that the deeper strata were protected by the absence of free oxygen. We now know that the active rays have scarcely any power of penetrating organic films, and that this is the true explanation of the limitation of the sterilizing effect to the surface layers of the culture.

In retrospect, this work of Downes and Blunt seems directly suggestive of the necessity of exploring the more refrangible regions of the spectrum, with a view to locating the active rays. It is, therefore, surprising to find that the seed they sowed fell on relatively barren ground. It is true that much work was done, in the eighties, on the effect of light in killing micro-organisms, bacteria, moulds and their spores,[2] but to venture a Hibernicism, none of these workers saw the invisible rays as the true source of the action they were studying.

It was not till 1892 that the clear indications of Downes and Blunts' work began to bear fruit. In that year Marshall Ward published the results of experiments on cultures of the Anthrax Bacillus and of other microbes exposed to the rays from the sun and from the carbon arc.[3] Ward reported that, while some bactericidal action was produced by the more refrangible rays of the visible spectrum, by far the most intense action was due to the invisible, ultraviolet rays.

A thin sheet of glass, interposed between the source of the radiation and the test culture, sufficed to cut out practically all the lethal rays, while a sheet of transparent quartz had no such effect. Now glass transmits the whole visible spectrum and the longest ultraviolet rays down to μμ 340, while quartz is transparent to both the visible rays and the ultraviolet down to 185 μμ. The conclusion was obvious: The germicidal action is concentrated in the ultraviolet, somewhere between μμ 340 and μμ 185.

[2] Arloing, Compt. rend. *100,* 378, and *101,* 511; Duclaux, 1885; Roux, Ann. Inst. Past. 1887.

[3] Marshall Ward, Proc. Roy. Soc. *53,* 393.

Ward discovered that the action was just as vigorous in the absence of free oxygen as in the air. This has, since, received ample confirmation. Oxygen, in the free state, is, therefore, not necessary for the sterilizing action of ultraviolet rays.

In this effect of exposure to sunlight, Ward recognized the most potent agent in the self-purification of rivers. It did not escape him that there was a possibility of putting his discoveries to a practical use and, although he did not realize their full potentialities, he went so far as to suggest that the naked arc should be used for the disinfection of small enclosed spaces, such as railway cars. Later, in collaboration with Lodge, the same worker established, in a more precise and positive fashion, that the bactericidal action was resident in the rays of the ultraviolet, which they used in "isolated" condition.

Other workers followed along the same lines, without notably adding to our stock of knowledge more than a confirmation of their predecessors' conclusions. It would be tedious and it is unnecessary to enter into details of their researches. This work of Ward and of his immediate successors may be said to close the first or qualitative period of research in ultraviolet sterilization. Ambitious attempts to replace the qualitative generalizations of their predecessors by a more precise quantitative statement of data were made by Bie and Bang. Each of these observers took pains to measure and to record the intensity of the radiation they employed. Bie's most valuable contribution was the use of liquid absorption filters to isolate, for study, particular regions of the spectrum. These filters consisted of colored liquids contained in parallel-sided transparent tanks. The thickness of the liquid was three centimeters.

The following filters were used:

1. One per cent aqueous solution of quinine sulfate: passing the visible spectrum.
2. Five per cent potassium chromate: passing red, orange, yellow and green.
3. One and one-half per cent potassium bichromate: passing red, orange, and yellow.
4. One-half of one per cent fuchsin: passing only the red.

The intensity of the radiation was measured by the degree of darkening of "Aristotype" (Collodio-chloride of silver) paper. Theoretically this can scarcely be considered satisfactory, because the sensitiveness of such paper is very unequally distributed through the spectrum, visible and invisible. A better idea of the energy employed is afforded by the specification: A carbon arc, amperes 35, volts 45 (about 600 C.P.); the light being concentrated by a Finsen apparatus and directed so as to fall normally on the surface of the culture under investigation. The organism used was the Bacillus prodigiosus.

The bactericidal effect of the more refrangible rays was confirmed, and it was shown to increase steeply with the decrease in wave-length. On long exposure, only, was any germicidal effect obtained by the action of the middle region of the visible spectrum. Pure red, on much

prolonged exposure, gave only a feeble retardation of growth and, apparently, exercised no lethal effect on the bacteria.

Bang, a colleague of Bie, improved on the latter's technique in the following ways: the use of quartz whenever it was desired to pass the ultraviolet: the accurate determination of the absorption of all apparatus: the elimination of most of the heat rays: the working at a determined temperature.

The method used was a hanging drop of bacterial suspension on the lower surface of a quartz plate: the quartz plate formed the lid of a "moist chamber." The temperature of the chamber was kept constant by a thermostatically controlled water-jacket. The arc, voltage and current were as in Bie's experiments: the distance twenty-eight centimeters: the angle of emission 45° to the axis of the carbon: between the arc and the object was interposed a water layer 25 millimeters thick, enclosed by quartz plates.

Some of the observations made by Bang were:

1. At 30° C. a culture of B. prodigiosus three hours old was killed in 60 seconds.

At 30° C. a culture of B. prodigiosus 10-15 hours old was killed in 210 seconds.

2. At 45° C. a culture of B. prodigiosus three hours old was killed in 15 seconds.

The reaction, therefore, in the conditions of Bang's experiments, seems to possess a positive thermal coefficient;[3a] an increase of 15° doubles the velocity.

In the same conditions, an older culture, of a nonsporing organism, is more resistant than a younger one. Is this latter result due to an increased resistance developed by the older bacterium? This seems unlikely, for in a 10-hour culture, most of the individual organisms are young,—the result of active cell division. Is it due merely to the greater numbers of the bacteria, giving more material to be acted upon and increasing the turbidity, and, therefore, decreasing the penetration of the rays? Or is the increased resistance caused by some change in the medium, the result of bacterial metabolism?[4]

We now come to a series of experiments which contain the germs of two cardinal differentiations: it becomes apparent that not the whole,

[3a] See also: Thiele and Wolf, Arch. Hyg., *60*, 29; Chem. Abs. 1907, 1029; Contra: see Cernovodeanu and Henri: Compt. Rend. 1910.

[4] These questions might be answered by experiments along the following lines:

1. Count, by the standard methods, the number of bacteria in a 3-hour and in a 10-hour culture, respectively. Centrifuge the bacteria from the 10-hour culture and to the clear fluid add enough of the original 10-hour culture to bring the count up to that of the 3-hour culture. Expose to the rays as in Bang's experiment.

2. Centrifuge both 3-hour and 10-hour cultures; after washing the bacteria resuspend them, the 10-hour culture in the 3-hour broth and *vice versa*. Expose as before.

3. Centrifuge the cultures as before and, after washing, suspend the bacteria in water in such a manner as to have the same bacterial count in each suspension. Expose as before.

but only the middle part of the ultraviolet is endowed with strong bactericidal power and, also, that any therapeutic virtue possessed by the rays is likely to be due to tissue reaction induced by the more penetrating, longer ultraviolet, rather than to direct killing of pathogenic organisms in the tissues by the shorter, germicidal range of rays.

Up to the time of which we are now writing it was understood that the bactericidal action was most marked in the ultraviolet, slight in the blue-violet, negligible in the middle region of the visible spectrum and non-existent in the red.

In 1903, Bernard and Morgan, working in MacFadyen's laboratory at the Lister Institute, made an elaborate series of experiments which led to the following conclusions:[5]

1. The bactericidal action is practically confined to the region of the ultraviolet between wave lengths 329 μμ and 226 μμ (3287 Å and 2265 Å).

2. The rays defined in the preceding conclusion are possessed of so little power of penetrating organic matter that there is no hope of using their sterilizing action for killing organisms in the body tissues.

3. That the rays responsible for the known therapeutic effects of light are, also, probably chiefly ultraviolet rays, but of longer wave-length than 330 μμ (3300 Å).

Apparatus was set up as for photography of the spectrum of the carbon arc, except that in place of the photographic plate, there was substituted an "Agar" plate, superficially inoculated with a culture of Bacillus coli communis. The lenses, the prisms, the plates enclosing the cooling water, were all of quartz. The spectrum was projected on the inoculated surface for a definite time, and the plate was then incubated.

That part of the surface which had been exposed to the rays of wave lengths from 329 μμ to 226 μμ (3287 Å-2265 Å) alone showed any sign of bactericidal action. No action at all was observed on either side of the above limits, even when the slit of the spectroscope was wide open and the exposure prolonged to two hours.

Later workers, refining on the technique of Bernard and Morgan, have fixed these limits somewhat differently. The limits generally accepted at the present time are 296 μμ-210 μμ (2960 Å to 2100 Å).[6]

This is, however, a matter of detail. What is important is that Bernard and Morgan demonstrated the limitation of the bactericidal action to the middle region of the ultraviolet.

It is significant that the less refrangible edge of this region corresponds, fairly closely, with the average limit of the ultraviolet component of the sun's radiation, as it reaches the earth's surface. This, taken with the known bactericidal action of sunlight, would suggest that, although the isolated parts of the sun's spectrum have a negligible bactericidal action, they are when united as "white" light, capable of exerting an action on bacteria qualitatively similar to that of the middle ultraviolet.

[5] Bernard and Morgan, Brit. Med. J. 1903, Nov. 14.

[6] But see p. 242.

Bernard and Morgan tried out arcs of different metallic positive electrodes, and found that the cadmium and the iron arc were more efficient than the carbon arc.

The bactericidal effect was found to vary directly as the intensity of the radiation, and not as the current input. This is merely another way of confirming the known fact that the intensity of radiation rises more steeply, within working limits, than the amperage. They found that the active rays were completely arrested by thin films of agar medium,[7] as well as by the epidermis, stretched as a thin membranous filter.

An agar plate, superficially inoculated with B. coli communis, was exposed to the radiation coming from the arc after passing through cooling water, quartz plates, and through a thin stretched membrane of human epidermis. The exposure lasted two hours. No sterilizing effect was produced. In the absence of the epidermal filter, the same radiation produced a sterilization of the surface growth in eleven minutes.

It thus appeared that nothing was to be hoped for from the direct action of the rays in the way of sterilizing pathogenic organisms in the body tissues.

Nevertheless, therapeutic benefit, in bacterial disease, had been attributed to ultraviolet radiation. This matter belongs to the next chapter, where it will be discussed. Suffice it here to say that Bernard and Morgan found indications that some region of the ultraviolet, not that of the sterilizing rays, was capable of producing tissue reactions to which might be attributed the beneficial effects known to result from ultraviolet radiation.

These workers believed that they had shown an absorption, by the cooling water, of about 80 per cent of the active rays. With the superior technique afforded by the quartz enclosed mercury arc, this observation has been proved erroneous.

In consequence of the work of Bie and of Bang, and especially, of that of Bernard and Morgan, the questions with which we have to deal begin to present themselves as rather complex. It would be confusing to the reader to continue this review of the development in a strictly historical order. For the sake of lucidity, therefore, we will follow each branch of investigation more or less separately.

Spectrum Region of Bactericidal Activity.

Continuing with the mapping of the active regions of the ultraviolet, we find that the majority of workers have fixed the region of bactericidal activity in the region between the wave-lengths 296 μμ and 210 μμ (2960 Å and 2100 Å). Thus, Newcomer,[8] working with the bacillus of typhoid fever, gives the limits 280 μμ to 210 μμ, with zero

[7] The reader is reminded that "Agar medium" is not a simple gel of agar-agar. It contains added proteins and extractives and, sometimes, sugar. It is from these and not from the agar that the bacteria derive their nutriment. The agar is used merely as a solid, non-digestible support.

[8] J. Exp. Med. 1917, 841.

action at 297 μμ. Browning and Russ,[9] using agar surface cultures, a tungsten lamp, and a quartz spectrometer, give 296 μμ to 210 μμ, with a maximum at 280 μμ to 254 μμ. Cernovodeanu and Henri,[10] using a Cooper-Hewitt lamp and bacterial emulsions, found a maximum at about 280 μμ. Mashimo,[11] using agar surface cultures and a quartz spectrometer, found the bactericidal range to be from 295 μμ to 186 μμ, with a maximum at 275 μμ. Baynes-Jones and Linden [12] give 350 μμ to 185.6 μμ.

The differences reported may be explained as due to variations in technique, especially the following:

Surface cultures can be killed by rays of less penetration (i.e., of longer wave-length) than are needed for emulsions. This is reversed when agitation of the emulsions is practiced. Arcs of different electrodes vary in the position of their lines of emission, where the energy is concentrated. Temperature and hydrogen ion concentration have some effect.[13] But there are some aberrant results not so easily explained. Bang [14] using a carbon arc at 30 amperes, found that the maximum action occurs at 250 μμ.

More inexplicable are the results reported by Bazzoni [15] to the effect that the full radiation from sources of light containing waves below 250 μμ will kill bacteria, but that isolated ultraviolet ray regions (250 μμ to 280 μμ) will not affect bacteria, in a drop of water, in one hour's exposure. He states, further, that several hours' exposure is needed to kill bacteria with ultraviolet rays of 220 μμ to 225 μμ, even when the intensity of radiation is the same as that of the rapidly destructive full radiation. The destructive power increased with decrease in wave-length.

These findings of Bazzoni's are in flat contradiction with those of other workers in the following respects: Results with quartz spectrometer show bactericidal action even in sharply isolated bands of ultraviolet.[16] So far from increasing with decreasing wave-length, the action becomes progressively feebler on the more refrangible side of 275 μμ (or 250 μμ, if we follow Bang).[17] Bazzoni's results do not seem to have been confirmed, and, until this happens, they cannot be accepted, even with reserve.

For the present, we may regard the *practically available* bactericidal region as stretching from 296 μμ to 210 μμ, with a maximum between 280 μμ and 250 μμ.

Theoretical.

When we seek an explanation of this localized activity, we find the following relevant observations: In accordance with the laws of photo-

[9] J. S. C. I. 1917, 1146; Proc. Roy. Soc. 1917, 33; Chem. Abs. 1918, 187.
[10] Compt. rend. 1910, *150*, 52.
[11] Memo. Col. I. Sci. Kyoto, 1919, *4*, 1 to 11; J. S. C. I. 1921, 161 A.
[12] Bull. Johns Hopkins Hosp. 34, *11*, Jan. 1923. Cf. Bovie, Botanical Gazette, 1916, *61*, 1, on action of Schumann rays. See Addenda, Chap. 15.
[13] Thiele and Wolf, loc. cit.; Baynes-Jones and Linden, loc. cit.
[14] Compt. rend. 1912, *155*, 315.
[15] Am. J. Pub. Health, 1914, *4*, 975.
[16] Browning and Russ, loc. cit.; Mashimo, loc. cit.
[17] But see Baynes-Jones and Linden, loc. cit.

chemical action, the rays which kill must be those which are absorbed by the body acted upon. In view of the Law of the Conservation of Energy, this may seem a truism. Exemplification may, nevertheless, be worth while.[17a]

Ultraviolet rays were passed through emulsions of bacteria in water, and the spectrum of the emergent rays was photographed. Absorption bands were found in the region of the bactericidal rays. The bacteria had absorbed the rays which killed them.[18] Henri [19] showed that the region of the ultraviolet endowed with maximum bactericidal power is that which is absorbed by protein. Further, the degree of action is almost exactly proportional to the extinction coefficient of protoplasm for those rays.

Pursuing this line of research, we next learn that, of the constituents of the protein molecule, the aromatic amino-acids, tyrosin and phenylalanin, have absorption bands between 248 μμ and 271 μμ. Following this clew, Harris and Hoyt [20] spread dry, pure cultures of Staphylococcus aureus, of Bacillus subtilis and of Bacillus mucosus capsulatus on glass cover slips. These were exposed to ultraviolet radiation in two sets of conditions: 1. Direct. 2. With interposition of a quartz beaker containing a one per cent solution of tyrosin. The result was to show that the absorption of the lethal rays by the tyrosin protected the organisms. Thus, B. subtilis on direct exposure was killed in 150 seconds: when protected by the tyrosin solution it survived exposure for 40 minutes. The times for the staphylococcus were 90 seconds and 40 minutes; those for B. mucosus capsulatus, 20 seconds and, at least, 10 mintes. All three organisms survived exposure for 3200 seconds when aminobenzoic acid was substituted for tyrosin.[21]

That it is the aromatic and not the aliphatic amino-acids that are attacked is indicated in similar experiments with leucin and alpha-alanin made by Houghton and Davis.[22]

These experiments do not afford conclusive proof that the lethal action of the ultraviolet is due to the effect on the aromatic amino-acids. Cocaine also protects against the rays, without undergoing, itself, any discoverable change.[23] Nevertheless, the evidence is cogent and, taken in connection with the effect on adrenin, so closely related to tyrosin, it sets up a strong presumption in favor of the hypothesis in support of which it is adduced.

An interesting expansion of this aspect of our subject is dealt with in some work of Dreyer (Mitteil. Finsen. Med. Lichtinst. *7*, 1904, cited by Cleaves, Light Energy, New York, 1904, 190). To understand the

[17a] See page 119.

[18] Browning and Russ, loc. cit.; Baynes-Jones and Linden, loc. cit.

[19] Compt. rend soc. biol., *73*, 323.

[20] Pathology, 1919, *2*, 245; Chem. Abs. 1919, 2384.

[21] As confirmatory evidence may be adduced the fact that adrenin (epinephrin) which is, chemically, closely related to tyrosin, is discolored and inactivated when exposed to ultraviolet rays. Houghton and Davis, Am. J. Pub. Health 1914, *4*, 224. Note, however, Savopol, Compt. rend. soc. biol. 1914, *77*, 458; Chem. Abs. 1917, 489.

[22] Loc. cit.

[23] Houghton and Davis, loc. cit.

drift of his ideas one must recollect that the photographic plate, normally insensitive to the yellow and green rays, can be made sensitive to them by dyeing the silver bromide of the emulsion with certain dyes, notably erythrosin.[24] Dreyer conceived the notion that this might apply to bacteria. Accordingly he suspended bacteria in a 1/5000 aqueous solution of erythrosin. On exposing the dyed bacteria to various ranges of light, through colored screens, he found that the middle region of the visible spectrum, normally innocuous, was now lethal. The following table of his results is quoted from Cleaves.[25]

TABLE 2.

Filter	Rays Acting	Time Required to Kill Bacteria[26]	
		Dyed	Normal
Quartz	Whole spectrum, including ultraviolet.	60 secs.	60 secs.
Glass	Visible spectrum.	10 min.	10 min.
Nickel Sulphate 5%	Red, orange, yellow, green, blue.	10 min.	10 min.
Pot. Chrom.	Red to green.	15 min.	More than 4 hrs.
Potassium Bichromate	Red to yellow.	25 min.	More than 9 hrs.

Before leaving this question of the relation between the radiation absorption capacity of an organism and the lethal effect of the rays absorbed, we must advert to the peculiar case of the fluorescent bacteria.

Fluorescence is due to the conversion of light waves from a shorter to a longer wave-length, i.e., from a higher to a lower frequency. A

[24] The characteristics of a sensitizing dye are: 1. That it is capable of dyeing the silver halide. 2. That the colored silver halide shall absorb the region of the spectrum for which it is to be sensitized, and, usually: 3. That the dye is fugitive to light. In fact, the absorption bands of the dye, when in solution do not usually coincide, exactly, with the region to which it sensitizes the plate. The explanation is to be sought, probably, in a shift of the bands when the dye is absorbed to the silver halide. Dyes which sensitize to the red and orange are blue, e.g., cyanins and isocyanins. Those for yellow and green are purple (deep pink), e.g., erythrosin; those for the violet and near ultraviolet, yellow.

[25] Loc. cit.

[26] Note the high dilution (1/5000) in which Dreyer used his dye. It is an extremely important point in technique, often disregarded in this kind of work, that the dye must not color the medium in which the particles (silver bromide or bacteria) are dispersed. If this is neglected the medium will absorb the rays before they can reach the particles. To provide against this, one of the following methods must be adopted:

1. Extreme dilution of the dye, as used by Dreyer. The particles, having high affinity for the dye take it all up.

2. Thorough washing after staining. Preference is given to dyes that are easily washed out of the medium.

For bacteria, the following method is recommended by Nolan: Centrifuge the bacteria; wash thoroughly, centrifuging between washings until the washings are protein-free; dye and then wash as before until the washings are free from color.

fluorescent substance is a kind of step-down transformer for "electromagnetic" waves of light. Certain bacteria exhibit this phenomenon in a remarkable degree. Burge and Neill [27] observe that fluorescent bacteria are relatively resistant to the destructive action of ultraviolet rays. The cause is, apparently, the conversion, in fluorescence, of the lethal short-wave rays into longer innocuous rays.

Would it not be interesting to know whether these bacteria, when exposed to the extreme ultraviolet, beyond 210 μμ, would step these rays down to rays of longer wave-length within what is now considered the operative lethal range? [27a]

The question of the velocity of the reaction and the thermal coefficient [28] is, in the nature of things, one which can be answered only for each determined set of conditions.

If we accord to all observers the same weight, we may, perhaps, be justified in adopting the following as a provisional approximation:

1. When a fairly dense suspension of bacteria is exposed in a thin layer to the action of the ultraviolet, there is a definite, positive thermal coefficient of such an order that a rise of 15° C. doubles the velocity of the reaction.[29]

2. When the medium is water and the bacteria are widely dispersed in it, there is no sensible thermal coefficient under usual conditions.[30] Thus v. Recklinghausen says that the bacteria in a block of ice are as rapidly killed as in water at ordinary temperatures, when the intensity of radiation is the same in both cases.

3. The velocity of the reaction is increased by increase in hydrogen ion concentration beyond p_H 4.6.

There was a natural temptation to explain the lethal effect of the ultraviolet as due to the action of germicidal substances produced in the medium. The favor-candidates for this rôle were hydrogen peroxide and ozone, especially with those who believed free oxygen essential to the action. But quantitative experiments soon dispelled the notion. It is true that ozone and hydrogen peroxide are formed when ultraviolet rays act on water and on moist air. But the quantity produced is so infinitesimal as to have no possible germicidal effect. Even after an exposure of water for 10 to 12 hours the amount of peroxide produced is scarcely detectable.[31]

There can be no reasonable doubt, in view of the facts already cited, that the action is a direct one, due to the absorption, by the protein molecule, of the lethal rays, and the probable mechanism according to Glaser is resonance setting up disruptive vibration.

[27] Amer. J. Physiol. 1915, *88*, 401; J. Chem. Soc. 1915, Abs. *108*, i, 1042.

[27a] In considering this question the work of Bovie with Schumann rays, see Chap. 15, Addenda, or Botanical Gazette, 1916, *61*, 1, should not be overlooked. Rays in the Schumann region may be even more lethal than those in the zone which we have been discussing but their effectiveness from a practical standpoint may be slightly due to the fact that most substances, including air, suppress them by absorption.

[28] See Chap. 13.

[29] Bang, loc. cit.; Thiele and Wolf, loc. cit.

[30] Cernovodeanu and Henri, loc. cit.

[31] Courmont, Chem. Zeit. 1911, *35*, 806; J. S. C. I. 1911, 1027. Houghton and Davis, Okerblom, v. Recklinghausen and others have made the same observation. The formation of hydrogen peroxide but not its germicidal effects is described in Chapter 7.

Specific Variation in Resistance.

While all microscopic living forms can be killed by exposure to the ultraviolet, they exhibit varying degrees of resistance, either inherent, i.e., specific to the organism, or extrinsic, i.e., due to variations in the conditions of exposure. Among themselves bacteria show considerable, and, to some extent, characteristic variations of resistance from species to species. But an attempt to render these variations available for differentiation of bacteria was unsuccessful.[32]

As examples of the application of these facts to produce differential, or preferential sterilization may be instanced the following:

"Sterile" (vaccinia) virus is produced, according to one proposal,[33] by exposing the virus to the ultraviolet rays sufficiently to kill the harmful foreign organisms, without injuring the more resistant virtue.[34] When milk is incompletely sterilized by exposure to the ultraviolet, it is found that the noxious bacteria are more affected than the relatively desirable members of the lactic acid group.[35] Spores are somewhat more resistant than the vegetative forms.[36]

But the ratio of the resistance of spores to sterilization by the ultraviolet, and the resistance of the vegetative forms to the same agent is much smaller than is the ratio when it is a matter of chemical sterilization. Thus von Recklinghausen states that while spores are twenty times as resistant as the vegetative forms to the action of chemical germicides, they are only three times more resistant than the vegetative forms to the ultraviolet rays.

Reports on molds are conflicting. Some workers state that they are killed by exposure to ultraviolet radiation without much difficulty.[37] Others report that molds are killed, by ordinary exposures, only when present in very small amounts.

The physical properties of molds are such as to render difficult the task of making experiments on them in determined standard conditions. Moreover their conditions at different periods of their life history are diverse.

It is noteworthy that molds have considerable mechanical protection in the form of fatty or waxy secretions. This may shield them from the radiation. Nolan observed a mold (Mucor mucedo) growing freely on the surface of a 1/1000 aqueous solution of mercuric chloride. He showed this, as a curiosity, to Lister, who gave the explanation in terms of a waxy protection, and said that he had been led to investigate the matter by a similar happening during his early work on antisepsis. Among the workers who have reported that molds are killed by the ultraviolet are Fairhall and Bates.[38] Their observation was made in

[32] Browning and Russ, in Browning, Applied Bacteriology, Oxford Univ. Press, 1918, 150-157.
[33] German Patent 314,859, 1914.
[34] J. S. C. I. 1920, *39*, 312 A.
[35] Houghton and Davis, loc. cit.
[36] Lagerberg, Z. Immunität. 1919, *28*, 186; Chem. Abs. 1919, 2385.
[37] Houghton and Davis, Amer. J. Pub. Health 1914, *4*, 224; Fairhall and Bates, The Cotton Oil Press, 1921, 33.
[38] Loc. cit.

the course of experiments on the sterilization of oils. This may have a bearing on the matter just alluded to. If the mold has a waxy or oily coat, and if it is immersed in oil, it is natural to suppose that conditions permitting of the sterilization of the latter would permit of the penetration of the waxy or oily coat of the mold. This might, indeed, be absent or be dissolved in the case of a mold in oil.

Extrinsic Obstacles to Sterilization.

More important than the inherent resistance of organisms, as an obstacle to the practical application of ultraviolet radiation for sterilization, are the low penetrative power of the bactericidal range, and the avidity with which the rays are absorbed by organic substances (which

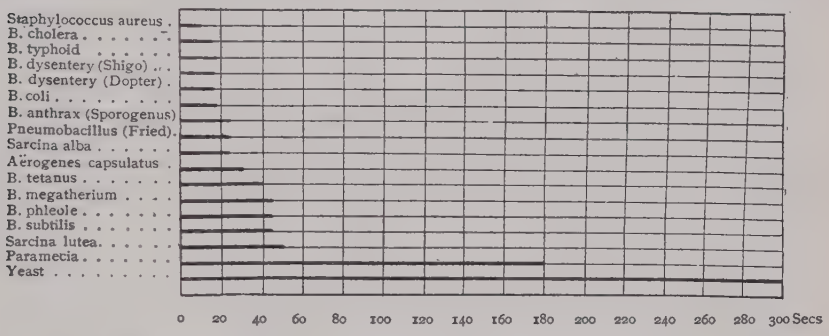


FIG. 57.—Time in Seconds Required to Destroy Various Organisms at a Distance of 200 mm. from a quartz mercury lamp operating at 66 volts and 3.5 ampères.[38a]

is merely the other aspect of the same phenomenon). Therefore the following commonly occurring conditions are inimical to successful application of the method:

1. Turbidity.
2. The presence of organic matter, protein, extractives and the like.
3. The presence of fats and oils.

Note that color, so important in the visible range, is *per se* of little or no importance when working with the ultraviolet. Quite dark wines are readily sterilized, and dark, aqueous solutions of Bismarck Brown afford no protection to bacteria suspended in them.[39]

Of the listed inhibitory conditions none is more important than the presence of organic matter in solution. It is, at once, the most powerfully obstructive, and the one which is most difficult to provide against by mechanical means. There are many conditions in which sterilization by ultraviolet would be the method of choice were it not ruled out by the difficulties created by organic matter, especially in solution. Conspicuous instances are liquid media (bouillons) and serums. Under

[38a] Von Recklinghausen.
[39] Houghton and Lewis, loc. cit.

the limitations of practical application, these cannot be sterilized by radiation. In some instances, moreover, undesirable side effects are produced, e.g., an irritating taste in milk.

Turbidity is easily (and literally) sidestepped. If the degree of dispersion is high (fine particles) and the density of the turbidity low, it suffices to agitate the liquid undergoing treatment, so as to bring all sides of the particles into the rays. This is the case with most natural waters. If the dispersion is low (coarse particles) and the degree of turbidity high, it will be necessary, in addition to agitation, to have recourse to exposure in thin layers. There are innumerable methods devised for this purpose. Most of them have been made the subjects of patents, and the more important and illustrative types will be dealt with later in this chapter.

Analogous to turbidity is the presence of air bubbles. These cast a protecting shadow. They are best dealt with by preventing their formation.

Oils and fats, though they protect organisms, to some extent, from the action of the radiation, especially when dispersed in globule form, can themselves be sterilized if irradiated in thin layers. During this process they undergo certain other changes which will be mentioned presently.

Sources of Ultraviolet Rays for Sterilization.

For the purpose of sterilization, the older methods of producing the ultraviolet radiation are mainly of historical interest. The quartz-enclosed mercury arc has superseded all the other forms, including the carbon and metallic arcs, the tungsten lamp, and even the sun. (See also Chapters 2 and 3.)

The quartz lamp is made in two distinct forms: air-cooled and water-cooled. The former is less well adapted for sterilization than the latter. The reason is that owing to the high temperature of the air-cooled lamp the arc is surrounded by vapor of mercury. This absorbs to a considerable degree the bactericidal rays. The water-cooling condenses these vapors, or prevents their formation, this permitting of the passage of the active rays of the middle ultraviolet. Care has to be taken in designing these lamps that the cooling is not excessive, as this would lower the intensity of the radiation. The superiority of the water-cooled lamp is not disputed in therapy and other small scale applications of the bactericidal or, to give them their more generalized name, the abiotic rays. On a larger scale, as for the sterilization of water, the advantage is less marked probably because an "overdose" is the rule rather than the exception. Von Recklinghausen expresses, in fact, a preference for the air-cooled lamp for such work.

Side Actions.

This closes the general review of the question of sterilization by ultraviolet rays. Before dealing with specific applications of this knowledge, we must advert to some side actions of the rays which are met

with in practice. Of these some are desirable and some not. The former are the object of special methods to develop them; the latter, of means for their prevention.

First we must refer to an alleged phenomenon of dubious authenticity and still more doubtful explanation. This is the pre-sensitization of water, the so-called "residual effect."

"If to a sample of water that has been sterilized with the rays, fresh live bacteria are added, within an hour's time practically 90 per cent of the organisms are killed. The action is called 'residual effect.' It has found important clinical usage and is a unique finding that merits study and research." [40]

Cernovodeanu and Henri [41] were unable to detect any trace of such residual action. Perhaps they operated with water free from bacteria, alive or dead, while Pacini and Decker speak of water that has been sterilized. The latter might, of course, contain products of the disintegration of bacteria.

It is conceivable that these products might show some slight bactericidal action. But for 90 per cent of the bacteria to be killed by this action would mean a very meagre dose of fresh organisms.

In this connection it is worth recalling that Roux [42] reported that bouillon, exposed for some hours to full sunlight, would inhibit the generation of spores of B. anthracis, though still capable of successful use for the cultivation of vegetative forms.

A number of fallacies lurk in such conditions. Hume and Smith found that they had been deceived when they believed that their experiments had shown a "residual effect" in irradiated air (see chapter on Therapeutic Applications). The quartz container, or some other part of the environment, may have been the source of the supposed residual effect in water. Moreover, great caution has to be observed to distinguish between agglutination and destruction of bacteria, in counting colonies. The important therapeutic application referred to by Pacini seems to be the use of irradiated medicated (e.g., borated) water for vaginal injections. This can scarcely be described, fairly, as an application of irradiated water.

Among the effects that we have to consider is one which has been reported by several observers. This is a modification of bacteria, short of sterilization, produced by the ultraviolet. Generally this is an attenuation, such as is well known to be produced by other means, or, in the case of colored bacteria, a change in the pigment forming function.[43] But actual mutations have also been reported. By the action of ultraviolet radiations upon B. anthracis, Madame Henri [44] claims to have produced two new forms, both stable. One of these sets up an infection different from that of anthrax.

[40] Pacini, Outline of Ultraviolet Therapy, Chicago, 1923; see also Decker, Chem. & Met. Eng. 1920, *22*, 639; Walker and Pryer, Amer. J. Pub. Health 11, 1921.

[41] Compt. rend. 1910, *150*, 52.

[42] Ann. Inst. Pasteur 1887, *1*, 445.

[43] Arloing, loc. cit.; D'Arsonval and Charrin, Compt. rend. 1894.

[44] Electr. Rev. 1914, *74*, 768.

Among the potentially useful side actions of the ultraviolet on bacteria are the effects reported by Eberson.[45] This worker exposed types of meningococci to ultraviolet radiation, and studied the changes in the antigenic properties, i.e., in the power of exciting, in animals, the formation of defensive antibodies. The result showed that the treatment had diminished the virulence of the organism, but had increased the antigenic power. This suggests a method for building up an immunity by successive injections of organisms irradiated for regularly diminishing periods of time. There is evidence that a few strains, or perhaps a single strain of bacteria, may suffice for immunizing against a heterogeneous group of types.

It is instructive to consider together the two next described sets of experiments.

Cernovodeanu, with Henri and Baroni,[46] found that an emulsion of tuberculosis bacilli was readily sterilized by the ultraviolet. Tuberculin was inactivated by the same exposure.

Stassano and Lematte [47] found that while bacteria were readily killed by the radiation, their agglutinins, toxins and enzymes were as active as those of a living culture.

There is no contradiction here. The difference is due to the fact that the tuberculin here spoken of is an excretion, it exists in the medium surrounding the bacteria, while the bodies referred to by Stassano and Lematte are internal secretions of the bacteria, in the bodies of which they exist and are thereby protected from the action of the rays.

In strict concordance with the observations on tuberculin are those made on the oxidases of milk by Romer and Sames, the lipolytic ferments of oils by Fairhall and Bates, the complement of serum,[48] the toxin of lamprey serum,[49] diphtheria toxin,[50] all of which were inactivated by exposure to the ultraviolet radiation.

Scarcely any of these side effects seem to have received important practical application.

It is otherwise with the effect produced by ultraviolet on young wine. According to Henri, Helbronner and von Recklinghausen [51] the taste and color of the wine are changed and it quickly (in a few minutes) assumes the characteristics of old wine. Before the war this method of "ageing" wine was making substantial headway in France.

Exposure to ultraviolet radiation coagulates the "coagulable" proteins; some are coagulated in neutral or even in alkaline solution, while others require acidification. In all cases the reaction is accelerated by

[45] J. Immunol 1920, *5*, 345; Chem. Abs. 1920, 3273.
[46] Compt. rend. 1910, *151*, 724.
[47] Compt. rend. *152*, 623. Ultraviolet rays are reported by Pentimalli, Sperimentale 1924, *78*, 719; Chem. Abs. 1925, *19*, 1902, to be without action on the growth of chicken sarcoma.
[48] Bovie, J. Med. Res. 1918, *38*, 335.
[49] Kopaczewski, Compt. rend. soc. biol. 1917, *80*, 884.
[50] Lowenstein, Vienna Z. exper. Path. Ther. 1914, *15*, 279.
[51] U. S. Patent 1,130,400, March 2, 1915.

acidification.[52] This observation is in line with the more recent work of Baynes-Jones and Linden,[53] which showed that the bactericidal action was accelerated with increase of hydrogen ion concentration beyond *p*H 4.6.

The only proposal to make commercial application of this coagulating power that one can discover is that of Monvoisin, Barret and Robin.[54] Freshly killed meat is exposed to the ultraviolet, with a view to sterilizing the surface and to harden it, before desiccation.

Special Applications—Water.

At one time irradiation by the ultraviolet bid fair to be the method of choice for the sterilization of water on the large scale, and several important installations have worked with entire satisfaction.

The advantages of the method are evident. The water itself undergoes no change. The matters in solution and the air, both of which give to water, as a beverage, its pleasing qualities, are retained. An overdose is impossible. The cost is not prohibitive. The sterilization can be made as complete as desired.

Nevertheless, of recent years the method has declined in favor, not because of any disappointment in its performance, but owing to the competition of cheaper, and, in some respects, simpler chemical processes: chlorination for potable water, coppering for swimming pools.

Whether sterilization by ultraviolet will regain its position or not it would be hazardous to prophesy. There are, however, several fields of usefulness for the method in smaller scale operations, where the chemical methods are objectionable and, especially, where an overdose would be injurious.

Among these small scale operations are: the preparation of water for surgical purposes; the sterilization of water for bottling, or for the supply of small consumers, such as individual houses; the sterilization of water for washing butter, for the margarine industry and, in general, wherever the water is to be incorporated in food; the sterilization of water on shipboard, especially on ships navigating inland waters.

The discussions in the general part of this chapter have shown what are the conditions of successful operation and what are the main difficulties in the sterilization of water by irradiation. We shall first take up in turn each of these, showing how the proper conditions have been secured and the special difficulties met. After this we propose to examine, in more detail, some concrete applications.

Turbidity.

We have already learned that turbidity is a serious impediment to the satisfactory operation of the ultraviolet rays in sterilization. This is, therefore, the first matter to be considered, when the sterilization of a water is contemplated. If the degree of turbidity is high, as in the

[52] Dreyer and Hansen, Compt. rend. 1907, *145*, 234; J. Chem. Soc. 1907, i, *92*, 883.

[53] Loc. cit.

[54] British Patent 22,669, Nov. 17, 1914.

case of the water of a muddy river, there is no need to make any estimate of the amount of matter in suspension: we proceed at once to employ some method of clarification prior to irradiation, but if the water is only slightly turbid, or if it has already undergone some preliminary clearing, we need some method of testing the degree of remaining turbidity. Several kinds of apparatus on the market are available. In practice the Tyndall effect is relied upon. This is produced by projecting a beam of light through the water, at right angles to the line of sight and observing the path of the beam against a dark background. The greater the turbidity the brighter the illumination of the path of the beam. This method is made quantitative by refinement of the apparatus and the use of standards of turbidity.

Some natural waters are clear enough to permit of sterilization without preliminary clarification. Other waters are subject to variation in this respect; river waters from floods, lake waters from the disturbance of the bottom by storms.

Clarification is effected either by sedimentation, or by coarse filtration, or by a combination of the two, with or without the use of chemical coagulants, such as alum. This part of the treatment is foreign to our subject, and details of it must be sought in works on water supply engineering.

Water issuing from such treatment is in the same case as clear natural water. Both are liable to contain some residual particles. Therefore, to make assurance doubly sure, means are employed to cause every side of every particle to be exposed to the whole force of the sterilizing rays.

The following devices are intended to effect this:

1. Multiplicity of lamps, usually staggered along the path that is pursued by the water. This device is always combined with one of the others.
2. Rotation of the lamp. This has been proposed, but is scarcely practical.
3. Agitation of the liquid. Generally, this is effected as a part of the operation of other devices.
4. The formation of a vortex in the water by rapid rotation.[55]

   One form of such apparatus embodies a cylinder to contain the liquid to be sterilized. Through the center of this is passed a rod serving as a support for the ultraviolet lamps. In one type, the chamber is rotated at such a speed that the water will be thrown to the sides forming a hollow space in the center. In the other type, the vortex is produced by a propeller rotating in the chamber.

[55] Helbronner and von Recklinghausen, British Patent 30,397, Dec. 29, 1909; and Henri, Helbronner and von Recklinghausen, U. S. Patent 1,140,819, May 25, 1915. Note also Dornic and Daire, Chem. Ztg. 1909, 936; Tassilly and Gambier, Compt. rend. 1910, *151*, 342; Engineering Record 1912, 110; Scientific American 1917, 515; Otto, French Patent 421,296, Oct. 10, 1910; Otto, J. für Gasbeleuchtung u. Wasserversorgung 1913, 56, 528; Perkin, Trans. Faraday Soc. 1911, *6*, 199.

5. By the use of baffles of various types. These produce two effects, first they cause internal movements of the water; second, they form weirs over which the water flows in thin layers, in close proximity to the lamps. The varieties are endless. The following are typical: Nogier [56] describes a circular tube provided at intervals with partition plates or screens which alternately direct the current of water passing through the tube from the center to the periphery and *vice versa*. Quartz mercury lamps are situated in the tubes between the partition plates. Von Recklinghausen [57] describes weirs or baffle walls, over which the water flows in a thin stream, in close proximity to the mercury arc lamps.
6. By placing the lamps in a constriction of the flow channel, so that eddies are formed and the thickness of liquid is also much reduced.
7. By causing the water to flow over a corrugated surface in a thin film.[58]

Fouling of Lamp by Deposits.

Analogous to turbidity and similar in its deleterious effect on the efficiency of the apparatus, is the fouling of the lamp or of its casing by deposits. There are either atmospheric dust or mineral deposit from the water produced, presumably, by spray. The former can be provided against by adequate housing and regular cleaning of the lamps.

The formation of mineral deposits is avoided by causing the water to flow in contact with a quartz jacket enclosing the lamp. The jacket is provided to prevent excessive cooling of the lamp by the water. The space between the lamp and the jacket may be exhausted to improve its transparency to the rays.[59]

Electrical Failures, etc.

Failure of sterilization may occur through premature flow of the water, the lamp either being unlit or not yet emitting the necessary rays, the arc not being fully "built up." The same results may be due to accidental extinction of the lamp from injury or from current failure.

To provide against these dangers numerous automatic controls and signals have been devised. In an apparatus devised by Nogier,[60] the flow of water through the sterilizing vessel is controlled by a device installed in the electric circuit. This device includes a cylinder provided with an inlet and an outlet for the passage of the water, and with a piston. A rod with a conical end projects upward from the other side of the piston. When the electric current is switched off, a spring,

[56] French Patent 426,606, May 6, 1910.
[57] Note U. S. Patent 1,156,947, October 19, 1915.
[58] Von Recklinghausen, U. S. Patent 1,193,209, Aug. 1, 1916; J. S. C. I. 1916, 976.
[59] Henri, Heilbronner and von Recklinghausen, U. S. Patent 1,200,940, October 19, 1910.
[60] French Patent 420,281, Nov. 18, 1909; British Patent 9960, Apr. 20, 1911; J. S. C. I. 1912, 356.

acting on the piston presses the conical end of the piston rod into the funnel-shaped mouth of the inlet so that the flow of water to the sterilizing vessel is arrested. When the electric current is switched on, the piston is drawn upward by an electromagnet of soft iron, situated directly above the pillar before mentioned, and the water then flows to the sterilizing vessel at a rate which is proportional to the intensity

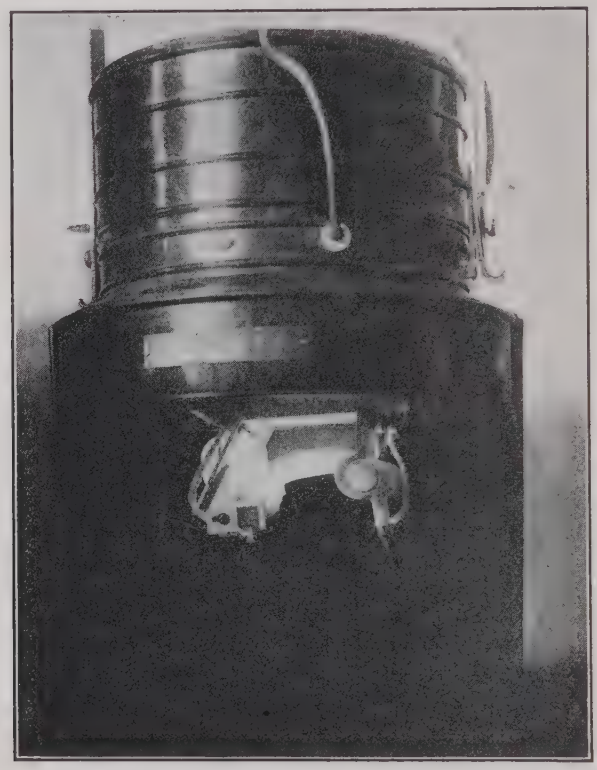


FIG. 58.—Ultraviolet Water-Sterilizer. There are many forms of small sterilizers for water, adapted for household use, swimming pools and other sterilizing operations.

of the electric current. Henri, Helbronner and von Recklinghausen [60a] describe a process for controlling the amount of liquid to be passed through the sterilizing chamber. For example, if the lamp becomes extinguished for any reason, the water is shut off, or on the other hand when the lamp is first started it takes some little time before it has reached its full power. In this case the water is allowed to flow slowly when the lamp is first put in operation, the rate of flow increasing until the control valve becomes wide open when the lamp has reached its maximum efficiency. See Figure 59.

[60a] U. S. Patent 1,150,117, August 17, 1915.

In apparatus of the type where a mercury vapor lamp, surrounded by a quartz chamber, is immersed in the liquid to be treated, a ball-float or similar device is proposed by Helbronner and von Recklinghausen[61] so that the operation of the lamp is prevented until the liquid rises to such a level in the tank, in which the sterilizing operation takes place, that the lamp is completely immersed in the liquid. The ball-float may be fitted in a small chamber on the pipe supplying the liquid to the tank containing the lamp.

A form of apparatus in which the lamp emitting the ultraviolet rays is suspended above a tank containing the water is also described by Helbronner and von Recklinghausen.[62] A helical quartz tube is mounted within the tank with its upper end just below the surface of the water, the lower end passes through the bottom of the tank. The

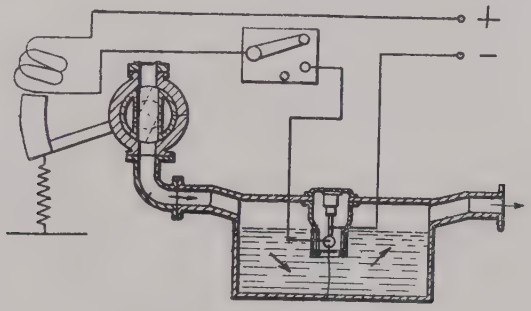


FIG. 59.—Automatic Control.

upper layer of water which is sterilized by the rays, passes into the helical tube and is discharged through a valve at the lower end. When the apparatus has not been used for some time, this valve may be closed until the tank is filled and the water overflows, carrying with it floating impurities.

In another apparatus of Helbronner and von Recklinghausen [63] the source of the ultraviolet rays is supported by a float mechanism (floats operating in chambers connected with the main conduit) so that a constant distance between the surface of the liquid and the source of the rays is automatically maintained. The lamp may also be mounted in a closed container fixed in a constant position above the liquid, the surface of which is automatically maintained at a definite level by means of a float valve capable of admitting air either under compression or at atmospheric pressure.

Where the liquid is admitted to the sterilizing chamber through a valve which is operated by an electromagnet in series with the lamp Helbronner and von Recklinghausen [64] suggest the use of an auxiliary

[61] British Patent 4,895, Feb. 27, 1911.
[62] British Patent 24,632, October 28, 1912.
[63] British Patents 28,067, Dec. 1, 1909, and 25,883, Jan. 24, 1910.
[64] British Patent 21,829, May 1, 1911.

valve so that any liquid leaking through the main valve when the latter closes owing to the lamp being extinguished, is conducted directly to a waste pipe and is thus prevented from entering the sterilizing chamber.

In another modification by Hellbronner and von Recklinghausen [65] the lamp is movably suspended in a quartz chamber from which the air is exhausted, the liquid to be treated being directed against the sides of the chamber. The outlet pipe for the liquid is provided with a valve which is operated by the flow of the liquid and regulates the working of the lamp.

Deterioration of Lamps.

Mercury arc lamps have been found to deteriorate in long use. There is no visual means of detecting this change and it is, therefore, necessary to test lamps under heavy duty from time to time. Public installations will always be under bacteriological control. It is necessary, in addition, to have some rapid method of testing the ultraviolet output of the lamps. Nolan suggests an actinometer consisting of two filter tanks; one of glass to contain a solution of quinine sulfate, which would pass the visible but not the ultraviolet rays; the other tank, of quartz, would hold pure water and would pass visible and ultraviolet rays alike. On these tanks, side by side, would be let fall, from a standard distance, the radiation from the lamp, at standard voltage and amperage. The rays would pass through the filters and fall on the surface of silver citrate paper. Exposure would be made for a standard time. The resulting darkening of the paper would be compared with a permanent standard. Such a test would take not more than a minute. That it would be not misleading is shown by the figure 60 in which the curve of darkening of silver citrate is seen to correspond closely with that of the lethal effect of the rays on the standard test organism B. coli communis. (For a description of actinometers of other types see Chapter 3.)

A considerable amount of the ultraviolet radiation is cut off by clouding of the quartz. This clouding is ascribed both to decomposition products from the electrodes and to changes in the nature of the quartz. Coblentz [65a] finds that the percentage of the total radiation which is below 4500 Å decreases from an initial value of 70 per cent to about 50 per cent after burning 1000 to 1500 hours. It should be particularly noted that this includes the strong groups of lines at 4360 and 4060 Å. Aston [65b] reports that a photograph of the mercury arc spectrum taken through the quartz of a burner which has been in use for 200 hours showed almost complete obliteration of all the lines in the ultraviolet, except the ones at 3660 and 3130 Å. However, none of the observations made during tests conducted by Nelson [65c] would indicate

[65] French Patent 424,369, March 12, 1910.

[65a] *Scientific Paper No. 330,* U. S. Bureau of Standards.

[65b] F. W. Aston, "Report on the Action of Sunlight on Aeroplane Fabric," T. 1019 British Advisory Committee for Aeronautics (1917).

[65c] Proc. Am. Soc. Testing Materials, 1923, *22,* II, 485.

a loss of effectiveness of the burners comparable with this until after 1000 to 1500 hours of service. Advantage has been taken by Nelson of the ionization of a zinc plate in vacuum by energy of wave-lengths in the region of 3000 Å and below, to discharge a gold leaf electroscope. The rate of discharge for the electroscope increases with the intensity

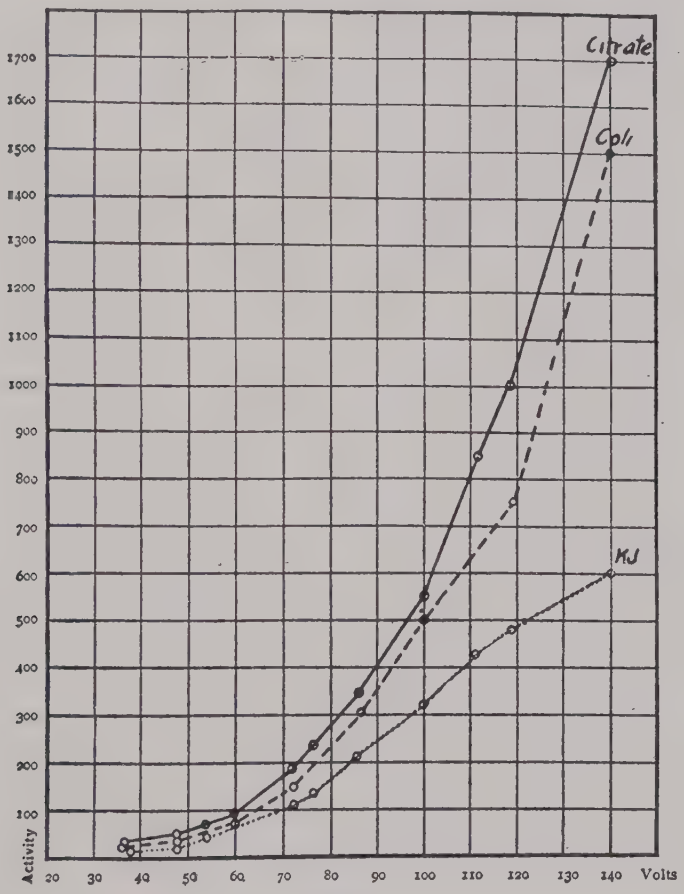


FIG. 60.

of the ultraviolet radiations and, by deducting the normal (dark) leak discharge, the relative intensities of the radiations are calculated as follows:

$$\frac{i_1}{i_2} = \frac{\frac{I}{t_1} - \frac{I}{t_0}}{\frac{I}{t_2} - \frac{I}{t_0}}$$

where

t_1 = time (seconds) to discharge electroscope under burner No. 1,
t_2 = time (seconds) under burner No. 2,
t_0 = time (seconds) to discharge when ultraviolet radiations are cut off by glass screen (dark leak),
i_1 = intensity of burner No. 1, and
i_2 = intensity of burner No. 2.

In one case a uartz mercury arc burner *A* had been in use for 500 hours and, within the accuracy of the observations, had lost none of its effectiveness in ageing tests on paints. Burner *B* was first used for 1600 hours, at which time its effectiveness had decreased very markedly. The deposit on the surface of the quartz was then removed in so far as possible by heating strongly with a blast (this treatment does not clear away all of the deposit) after which the tube was put back in service for 250 hours, making a total of 1850 hours. The relative intensities of the two burners in the ultraviolet region (3100 Å, and below) tested in the foregoing manner were found to be in the proportion of 1.7 to 1 when used at 220-240 volts and 6.5 amperes, indicating a decrease of about 40 per cent for the old burner.[65d]

Parkinson [66] has made a thorough research on the sterilization of water by means of ultraviolet radiation.

The source of water used by Parkinson is the Great Lakes, which he states is very satisfactory for use during the greater part of the year but in case of storms the water becomes turbid and is quite highly infected. Purification by filtration and chemical treatment therefore is necessary in order to insure at all times a pure drinking water. Owing to the purity of the water as it came from the purification plants it was necessary for Parkinson to pollute the water in order to have the bacteria count high enough for accurate results. Two types of apparatus were used by Parkinson, one being a small form having a 110-volt lamp, the other a larger apparatus having a 500-volt lamp. In both cases the apparatus was of the gravity type. In the smaller apparatus the lamp was suspended over the water, while in the larger one the lamp was entirely surrounded by the water during sterilization. Both pieces of apparatus were supplied with baffles, which were movable so that they could be shifted from one place to another or be removed entirely. After a long series of experiments with the baffles in various places and removed altogether, Parkinson concludes that baffles are not necessary in apparatus for the sterilization of water and that sterilization takes place almost immediately when the water comes in contact with the rays from the lamp. He states, however, that by using baffles a safety factor is obtained which makes sterilization a little more sure. When

[65d] Note Coblentz and Kahler on measurements of the component radiations from a quartz mercury vapor lamp, *Scientific Paper 378*, Bur. of Standards; Coblentz, Long and Kahler, *Scientific Paper 330*, and Coblentz and Fulton, *Scientific Paper 495*. The latter concerns a radio-metric investigation of the germicidal action of ultraviolet radiation.

[66] Thirty-third Annual Report of Provincial Board of Health of Ontario, Canada, 1914, 156.

using ultraviolet rays for the sterilization of water, it is impossible to impart an undesirable flavor to the water by over-treatment, consequently the only drawback to long treatment is the additional expense. In the location of apparatus for treating water Parkinson states that he had some difficulty from dust being deposited around the lamp, which caused its efficiency to be decreased. In order to obviate this, the sterilizing apparatus should be placed in some locality which is as free from dust as possible and it may prove advantageous to enclose the apparatus entirely in some special form of housing. In regard to the effect of slight turbidity on the sterilization of water, when treated with ultraviolet rays, Parkinson concludes that a small amount of turbidity is not detrimental, but in case turbidity is present the exposure must be slightly prolonged and the water should be agitated. Gross particles, however, should be avoided, inasmuch as they serve as a hindrance to the penetration of the light and perhaps throw shadows in which the bacteria are shielded from the light rays. When treating water with ultraviolet rays, Parkinson states that one noticeable feature is that the quality of the water so sterilized is very constant. There are no jumps of the bacteria count and in case the sterilizing apparatus is working steadily the bacteria count should remain practically constant, provided of course, the operating conditions, such as flow of water, voltage of lamp, etc., are maintained constant.

TABLE 3.

Adjustment of Baffles (Parkinson).

Horizontal Baffles	Opening in the Inclined Baffles	Turbidity, Parts per Million	Voltage	Percentage Bacterial Removal 18-22° C. Count	Percentage Bacterial Removal 37.5° C. Count
In place	¼ in.	1	350	99.84	98.7
In place	½ in.	1	350	99.3	99.2
In place	1 in.	1	350	99.8	99.67
In place	1½ in.	1	350	99.8	99.7
In place	2½ in.	1	350	99.84	99.72
Removed	¼ in.	30	350	97.5	98.5
Removed	½ in.	20	350	97.5	98.4
Removed	¾ in.	1	350	99.6	99.9
Removed	1 in.	20	350	98.7	99.0
Removed	1½ in.	30	350	98.5	98.6
Removed	2 in.	20	350	99.4	99.4

The following data from Parkinson's report illustrate concisely his conclusions in regard to several points which apparently are not definitely settled in the minds of various investigators. Table 3 illustrates the effect of the baffling system on the sterilizing apparatus used, together with the results obtained on removing the baffles. It will be noted from this table that there is no great variation in the bacteria content when using the greatest baffling effect possible and also the least with the apparatus at hand, although there is a high bacteria count at the intermediate stage which is probably due to some outside source.

In Table 4 Parkinson gives the results of data of an instructive

character as to the length of time necessary to cause sterilization. The samples taken at the various points are as follows:

"A" indicates a point just below the first baffle. "B" indicates a sample taken about midway between a set of baffles. "C" indicates a point close to the lamp just before the water passes out into the overflow. It will be noted from this table that there is almost complete bacterial removal when the water first comes in contact with the light.

TABLE 4.

Progress of Sterilization (Parkinson).

Sample Point	Average Bacterial Count			Percentage Removal			
	18-22° C. Count	37.5° C. Count	* Colon Fermentation	18-22° C. Count	37.5° C. Count	Colon Fermentation	Average Removal
Influent	730	200	1,230				
A	50	17.4	31	93.2	91.3	97.5	94.0
B	49.5	12.7	29	93.4	93.6	97.6	94.8
C	23	4.2	29	96.9	96.9	97.6	98.1
Effluent	26	16.4	20	96.4	96.8	98.4	97.2

* B. coli per 100 c.c. presumptive tests.

Table 5 shows the results of Parkinson's experiments upon the effect of turbidity, within certain limits, on the rate of sterilization. A large number of samples were used in each instance and conditions as to flow and voltage of lamp kept as near constant as possible. It will be noted from this table that there is practically no difference in the bacteria count at a given slow rate of speed in the turbid water and in that which is practically clear. Where high velocities were used, however, it will be observed that there is a difference in the bacteria count, depending upon the increase in turbidity and the increase in rate of flow, but a greater variation than this is caused by a change in the voltage of the lamp.

TABLE 5.

Effect of Turbidity on the Rate of Sterilization (Parkinson).

Rate of Flow in Gallons per Hour	Number of Samples	Turpidity Parts per Million	Voltage	Percentage Bacterial Removal		
				18-22° C. Count	37.5° C. Count	Colon Fermentation
3,000.....	40	under 1	350	99.81	99.82	99.88
	20	30	350	99.4	98.5	
5,000.....	65	under 1	350	97	94	97.4
5,000.....	20	40	350	94.9	91.3	99.46
5,000.....	20	under 1	325	87.5	75	96.3
7,000.....	74	under 1	350	86.8	94.4	96.0
7,000.....	20	10	350	91.8	86.4	97

Example of Large Scale Operation.

A description of the plant and operation of a large pressure type ultraviolet water sterilizer at Henderson, Kentucky, is furnished by

Smith.[67] The water delivered to the sterilizer is first passed through settling and coagulating tanks then through mechanical filters before reaching the sterilizer. The source of water supply is the Ohio River; the raw water is pumped into two coagulating basins 95 feet long, 30 feet wide and 16 feet deep, where it is stored for 4 hours, then into two baffled mixing chambers 25 feet long, 7½ feet wide and 17½ feet deep, and from there into six reinforced concrete filter units 17 feet long, and 13 feet 4 inches wide with a normal capacity of 625,000

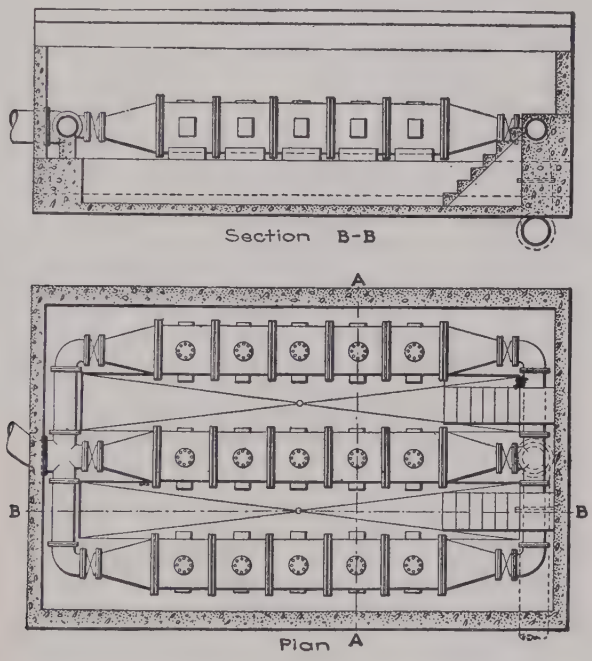


FIG. 61.

gallons each per day. The ultraviolet sterilizers consist of three legs each (Figure 61) comprising five units. The legs are connected in parallel and the entire equipment is connected in series with the pipe line leading from the filtered water basin to the storage for the city supply. Each unit has a lamp box inserted in the side equipped with a clear quartz closed end tube which projects into the body of the unit and around which the water is forced in a thin film by means of a baffle placed at 90° to the long axis of the sterilizer. The quartz tube is contained in a slotted opening in the baffle. See Figure 62. The lamp proper is a 220-volt direct current mercury vapor arc lamp and is designed to be automatically tilted by a special support located in the lamp box. The individual lamps are so connected that they may be adjusted

[67] Engineering News Record, 1917, 1021.

individually and are also connected to the main switch board, each lamp having a "tell tale" incandescent lamp and a warning bell to notify the

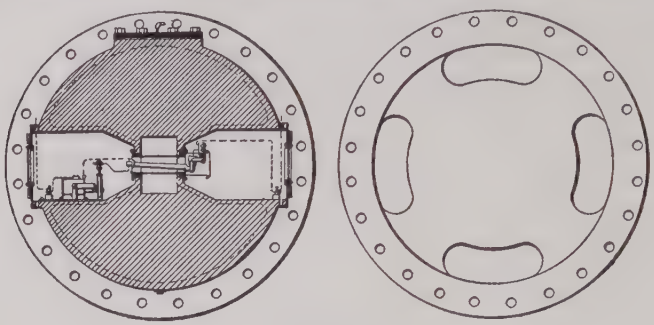


FIG. 62.

operator in case any of the lamps are not functioning properly. The following table shows the efficiency of the installation on which daily tests were made for over two months:

TABLE 6.

Typical Results, Bacterial Tests at Henderson Water-Purification Plant.

Sample	Total No. of Samples	Bacteria per c.c., 24-hr. Incubation — Total Bacteria — Maximum	Total Bacteria — Average	B. Coli — Maximum	B. Coli — Average
Raw	25	190,000	85,000	1000.0	276.0
Coagulated	25	1,200	820	100.0	45.0
Filter	70	320	80	1.0	0.35
Leg 1:					
Influent	52	95	32	1.0	0.260
Burner 1	48	30	16	0.8	0.215
Burner 2	48	20	8	0.8	0.200
Burner 3	48	16	6	0.2	0.136
Burner 4	48	6	2.10	0.1	0.090
Burner 5	54	3	0.31	0.0	0.000
Leg 2:					
Influent	53	75	36	1.0	0.310
Burner 1	47	50	12	0.6	0.273
Burner 2	47	20	6	0.8	0.18
Burner 3	47	7	5.20	0.4	0.117
Burner 4	47	6	1.80	0.1	0.07
Burner 5	54	3	0.38	0.0	0.0
Leg 3:					
Influent	54	95	25	1.0	0.326
Burner 1	47	55	14	0.8	0.240
Burner 2	47	19	9	0.8	0.21
Burner 3	47	12	4	0.4	0.110
Burner 4	47	6	1.60	0.1	0.06
Burner 5	54	3	0.42	0.0	0.0
Tap at pumps	34	11	0.39	0.0	0.0

Rate of pumping 2,200,000 gal. per day to 3,200,000 gal. per day, with little or no variation in results.

Turbidity of raw water varied from 130 to 880 p.p.m.

Filtered water usually clear with maximum turbidity of 5 p.p.m.

The rate of pumping was 2,200,000 to 3,200,000 gallons per day with little or no variation in results. The turbidity of the raw water varied from 130 to 880 p.p.m. The filtered water was usually clear with a maximum turbidity of 5 p.p.m. The plant operated for some months under a varying capacity of from 2,200,000 to 3,500,000 gallons per day at an expenditure of 92.5 kilowatt hours per million gallons.

Special Applications. Milk and Other Opaque Liquids.

Milk is the type of an opaque, organic liquid which requires sterilization and yet whose special properties render the operation of particular difficulty and delicacy. Its flavor must not be changed, and its food value must not be deteriorated. These are conditions which have not yet been realized by any process, and ultraviolet has proved no exception.

For years after the introduction of ultraviolet radiation as means of sterilization, the Patent Offices were flooded with specifications for processes for treating milk with the new agent, each more ingenious than its predecessor. We are relieved from the necessity of detailing all these methods by an admission wrung by experience from the most prolific of these inventors. Helbronner and von Recklinghausen,[68] speaking of the use of ultraviolet rays for the sterilization of milk, note that complete sterilization by this means alone is difficult and that the prolonged treatment necessary is quite likely to have deleterious effects upon the flavor and digestive qualities of the liquid. They therefore propose to use a combination of heat sterilization together with ultraviolet rays. It is stated that when milk is given a short heat treatment at a temperature above 60° Centigrade, the bacteria therein become so weakened that they are readily destroyed by ultraviolet rays. It is claimed that by this combination treatment the milk is not heated sufficiently to materially alter the flavor and that a very short exposure to the ultraviolet rays is sufficient to completely sterilize the liquid. (See Figure 63.)

In addition to the preheater there is illustrated in the figure another device which has found favor with those engaged in experimental work on sterilization of turbid liquids, i.e., the use of a rotating drum to pick up an exceedingly thin film of the opaque liquid. Milk and similar fluids do not form, by gravity or other usual methods, films of sufficient tenuity to permit of ready penetration by the rays. Hence the use of this device.

The removal of the sterilized product affords in the case of milk, yet another difficulty; this is the formation of particles of butter. Various devices have been employed to avoid this. In the following description of methods for sterilizing opaque liquids, some of these expedients are mentioned.

Von Recklinghausen sterilizes opaque liquids[69] by means of an

[68] U. S. Patent 1,141,046, May 25, 1915. The oxidases of milk are destroyed by ultraviolet rays while one form of reductase is unaffected. Sames, Milchwirtsch. Zentr. *6*, 462; Chem. Abs. 1911, *5*, 1468.

[69] Chem. Abs. 1916, 649; U. S. Patent 1,165,921, Dec. 28, 1915.

apparatus which exposes the liquid in a thin film, formed by passing the liquid between two plates spaced a short distance apart. The upper plate is composed of quartz or some other material transparent

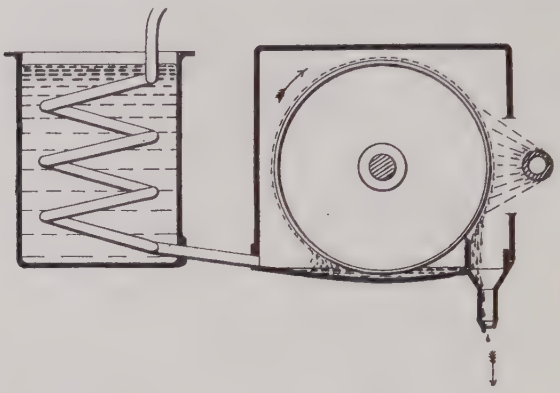


FIG. 63.—Apparatus of Helbronner and von Recklinghausen, for joint heat and ultraviolet treatment. Milk is heated to 60° C. by passing through coil shown on the left. A rotating drum, on the right, serves to expose the milk in a thin layer to ultraviolet rays.

to ultraviolet. The plates are held in place by thin sheets of tinfoil. The liquid to be sterilized is held in a container.

In another process for treating liquids with ultraviolet, Henri, Helbronner and von Recklinghausen [70] state that for sterilizing opaque or highly colored liquids such as milk, wine, etc., it is undesirable to

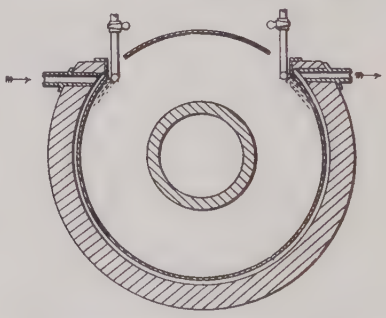


FIG. 64.—Water-Cooled Sterilization Apparatus of Henri, Helbronner and von Recklinghausen.

have the liquids exposed to the atmosphere while undergoing the sterilization treatment. In apparatus which they describe, the liquid to be treated is passed through a shallow chamber which is provided with

[70] U. S. Patent 1,140,818, May 25, 1915.

a cover of some substance, such as quartz, which is transparent to ultraviolet rays. The lamp is placed in such a manner that the rays may reach all parts of the container. In one instance the treating chamber is circular in cross section, the liquids to be treated being allowed to flow along the sides in a thin film. Provision is also made for cooling the apparatus. See Figure 64.

Another form of rotating drum apparatus proposed by Henri, Helbronner and von Recklinghausen [71] is shown in Figure 65. In treating milk, it is stated that where the scraper removes the liquid from the drum after being treated, particles of butter are quite likely to be formed and these may cause difficulty later. In one case the milk is removed from the roller by a jet of air, it being claimed that under

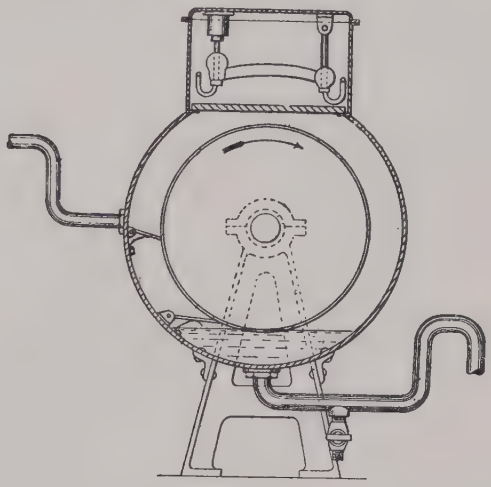


FIG. 65.

these conditions no butter is formed. It is also proposed to use a second cylinder to remove the milk after sterilization. (See Figure 66.) A further modification of apparatus for treating milk and other liquids is described by Henri, Helbronner and von Recklinghausen,[72] according to which the roller picks up a thin film of liquid, exposes it to the action of ultraviolet rays and in turn delivers it to a second roller; which gives it a further exposure. It is also proposed to arrange these cylinders in a gradually descending plane and then to expose in a gradually rising plane until the sterilized liquid is delivered at a point approximately on the same level as the point of entry. In such an apparatus the lamp is located in the center of this V-shaped formation. Various other forms of apparatus are described by Helbronner and von Recklinghausen [73] for treating opaque liquids with ultraviolet rays,

[71] U. S. Patent 1,068,898, July 29, 1913.
[72] U. S. Patent 1,052,818, Feb. 11, 1913.
[73] British Patents 12,948, May 27, 1910, and 18,458, Aug. 4, 1910.

the essential feature of each modification of the apparatus being that the liquid is caused to pass before the lamp in the form of a thin layer.

Special Applications. Pharmaceuticals.

The object of experiments by Lesure [74] was primarily to ascertain whether the sterilizing action of ultraviolet rays could be used in rendering medicinal preparations, particularly those used for injection subcutaneously or otherwise, aseptic. Twenty-four different liquids were exposed during 1 to 5 minutes or 15 to 30 minutes to the light emitted by a Cooper-Hewitt mercury lamp. The permeability to the

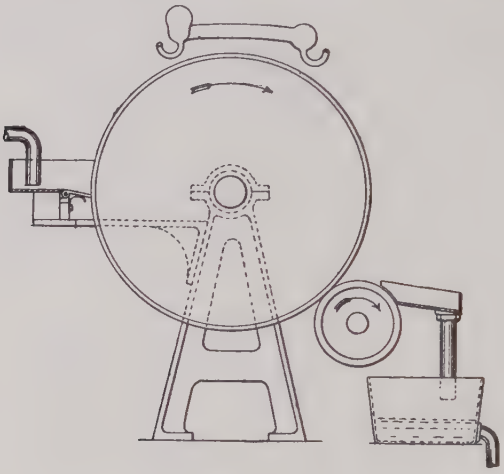


Fig. 66.

rays was observed by their effect on sensitized paper after passing through the solution under observation. In most cases the permeability was comparable to that of water, but for solutions of atoxyl, caffeine, eserine salicylate, apomorphine hydrochloride, gentiopicrin, or olive oil it was from 1/10 to 1/5 that in water. With solutions of mercuric iodide (in sodium iodide), quinine dihydrochloride, or quinine disulfate, it was practically nil. Certain of the solutions showed some change, thus silver nitrate, eserine salicylate, apomorphine hydrochloride and atoxyl all became colored after 5 minutes' exposure, while morphine hydrochloride, arbutin, and guaiacol cacodylate developed color after exposure of from 15 to 30 minutes. Olive oil was decolorized after illumination during 30 minutes, but there was no marked change in the constants of the oil. A solution of aucubin containing Bacterium coli was completely sterilized in 30 seconds, but a similar preparation of gentiopicrin was not thus sterilized after 30 minutes' exposure. In a second series of experiments it was found

[74] J. Pharm. Chim. 1910 (vii), 1, 569; J. Chem. Soc. 1910, *98*, ii, 739.

that olive oil became acid after exposure during 1 hour and that aucubin and gentiopicrin were decomposed and yielded reducing products after 3 hours. Arbutin became very much colored after 3 hours' illumination, due to the formation of quinol and its oxidation products. Methylarbutin behaved similarly, but required longer exposure before coloration occurred. Quinol became colored in 5 minutes, but methylquinol only after 30 minutes, and the solutions were then less permeable to the rays. Cocaine hydrochloride and pilocarpine hydrochloride did not appear to be affected appreciably even after three and a half hours, although the latter became slightly colored.

Special Applications. Oils and Fats.

Certain oils, such as olive, cottonseed, and almond oils, can be effectively sterilized by means of relatively short exposure (about three minutes) to ultraviolet rays. The germicidal or, indeed the abiotic power of the ultraviolet rays, is not restricted, according to Fairhall and Bates,[75] to vegetative bacterial cells alone, but extends to the spores as well as to certain molds, such as Penicillium, Aspergillus, and Mucor. Lipolytic enzymes in oil are sensitive to, and their action is inhibited by, exposure to ultraviolet rays. Except for a slight bleaching, the oil is unchanged physically and chemically by this exposure. Olive oil, when exposed for long periods of time, shows an increase in acidity, and this increase is directly proportional to the length of exposure.

Fats, butter and the like are sterilized by means of ultraviolet rays, according to Soc. Le Ferment,[76] in the following manner: The fat is spread in a thin layer on the surface of an endless band or on a drum. The movement of the band carries the layer of fat past a number of lamps which emit ultraviolet rays. These lamps are provided with a reflector. The fat is removed from the band by means of a scraper after it has passed the lamps. The band may be heated or cooled as desired.

Other Applications in Sterilization.

Quartz lamps are lowered into the cask and the light turned on for 15 to 30 seconds. It has been found inadvisable to continue the illumination longer than this brief period, in ordinary casks lined with pitch, since the resultant rise in temperature causes the formation of fumes of pitch.[77] From his experiments, Moufang,[78] concludes that by the application of ultraviolet rays for sterilizing barrels (by means of a specially constructed quartz lamp which could be inserted through the bung hole) the biological condition of pitched barrels may be greatly improved, but that perfect sterilization in a biological sense is not obtained.

[75] Cotton Oil Press, 1921, 33.
[76] French Patent 400,921, March 17, 1909.
[77] Scientific American, Aug. 28, 1920, 201.
[78] Kirm. a.d. Nahe Allgem. Z. Bierbrau Malzfab. 43, 151 (1915).

The observation by Nitzescu that ultraviolet rays have no deleterious effect on the properties of insulin led him to suggest this form of radiation as a means of sterilizing insulin solutions. By employing this method there is no occasion to use cresol for sterilizing purposes.[79]

Figures 67 and 68 illustrate apparatus used by Houghton and Davis [80] for sterilizing bacterial vaccines and other products. The material to be irradiated is contained in a glass flask B connected by a sterile glass siphon and rubber tubing to the trough C, placed directly beneath the arc. After exposure in the trough, the liquid passes

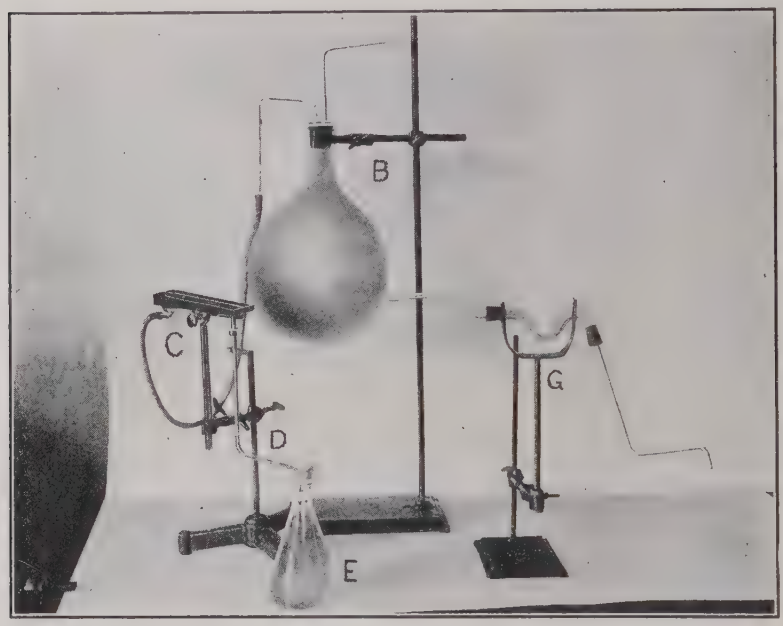


FIG. 67.

through the delivery tube D into a previously sterilized container E. A Cooper-Hewitt quartz mercury vapor lamp is used for irradiation and this is enclosed in housing, Figure 68.

A stimulation in the growth of beer yeast exposed to ultraviolet has been observed by de Fazi. For example, Saccharomyces opunitiæ becomes more vigorous under ultraviolet, provided the period of exposure be limited. Must of India fig in ordinary fermentation forms an abundant film over the surface, which increases from day to day. If, however, fermentation takes place under ultraviolet no trace of this film is visible. Saccharomyces cerevisiæ improves in activity by such irradia-

[79] Klin. Wochschr. 1924, *3*, 2343.
[80] Am. J. Public Health 1914, *4*, 224.

tion.[81] In conjunction with somewhat kindred methods developed by Fernbach [81] application has been made of ultraviolet on an industrial scale.[82] Thus the method is reported to have the following advantages over the ordinary method in the manufacture of beer: (1) the time of

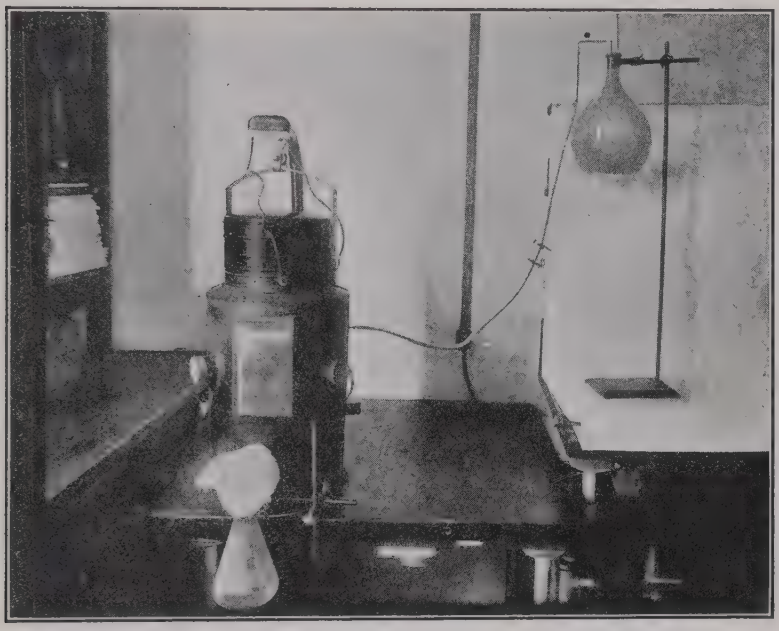


FIG. 68.

fermentation is 25 per cent less and that of maturation is 40 per cent less; (2) the quality of the beer is improved and it keeps better, and (3) the temperature can be kept low (4-6° R) in the principal fermentation and still the yeast will show a greater activity than at the ordinary temperature (6-8° R).

[81] Ann. chim. applicata 1915, *4*, 301; 1916, *6*, 221; 1917, *8*, 93.

[82] Alti congresso naz. chim. ind. 1924, 449; Chem. Abs. *10*, 950; *11*, 683; *12*, 402; J. Soc. Chem. Ind. 1916, 191; 1922, 992 A; 1925, B 257. Ann brasserie and distillerie 1923, 22, No. 7.

Chapter 13.

Biologic Effects and Therapeutic Applications. Part 1. Experimental.

Though the use of ultraviolet rays as a sterilizing agent has, of recent years, been somewhat on the decline, it is far otherwise with their application in the healing art.

From the epoch when the practice of ultraviolet radiation for the relief of disease was regarded, by most physicians, with indifference, bordering on suspicion, to the present day is but a short lapse of time, but it has brought an almost incredible expansion of the field for the therapeutic application of the ultraviolet. A list of the conditions for the treatment of which this method has been recommended reads like an official nomenclature of diseases, and it ranges from acne to zona, through housemaid's knee and the major psychoses.

Perhaps some of the present enthusiasm will be damped by further experience, but it is reasonably sure that the others will be strengthened and augmented.

Though not the logical, this is perhaps the most opportune point at which to allay certain fears. There is a rather widespread impression that radiation with ultraviolet light is capable of producing injuries comparable with those occasioned by the imprudent exposure to X-rays. These fears may be dismissed as illusory. Owing to the low penetration of ultraviolet rays, the local effects produced by heavy radiation are confined to the most superficial tissues—the skin and the conjunctiva—and the inflammatory reaction invariably subsides, and the lesions heal, on withdrawal of the exciting cause.

So far from serious burns being caused by ultraviolet rays, exposure to these very rays is becoming a favorable measure to relieve pain and to promote healing in ordinary burns, in X-ray dermatitis, and in sunburn.[1]

Much of the practice in ultraviolet radiation is empirical. This is, however, true of most important advances in therapeutics. Quinine in malaria, mercury in syphilis, iron in chlorosis, ipecac in dysentery, and the majority of our most valuable remedies entered the pharmacopœia, not through the portals of the pharmacologist's laboratory, but in consequence of accidental discoveries, of lucky guesses, and, not infrequently with credentials endorsed by alchemists, astrologers, magicians, and the medicine men of savage races.

[1] See account of Bach's heroic experiment on himself, page 297.

Experimental.

The laboratory workers are, however, breathlessly striving to catch up with the discoveries made by the practicing radiologists, and we must begin by reviewing their accomplishments.

Many of the reported results are in apparent contradiction. Sometimes this may be due to inaccurate observation and too hasty generalization. Usually, however, the cause of disagreement is to be found in want of conformity in experimental conditions. Much of the work already done cried aloud for repetition under standard conditions as to intensity and spectral region of the radiation, and as to the intervening media and the objects.

Two Kinds of Action of Ultraviolet.

We must habituate ourselves to thinking of the ultraviolet as having two disparate effects on living beings, which different actions are exerted by rays from regions of different wave-lengths.

The first kind of action may, for want of a better term, be called stimulative, since stimulation of biologic processes is its commonest expression.

The other sort of effect we may name lethal, since it is characterized by the death of the cells on which it is exerted. This is the effect with which we have already become familiar as the bactericidal action of the ultraviolet.

By a double wrench, to etymology and to established usage, these two kinds of action are referred to in the literature of ultraviolet therapy as "biologic" and "abiotic." [2]

The action which we have named stimulative is exerted by the ultraviolet from the limit of the visible spectrum to about 290 μμ (2900 Å). This corresponds closely to to the ultraviolet component of solar radiation at the earth's surface.

The lethal effect is exhibited by the rays of wave-lengths shorter than 290 μμ (2900 Å).

Lindner,[3] using a bottom-fermentation brewery yeast, found that the velocity of fermentation of dextrose was greatly increased by exposure to ultraviolet rays. Thus fermentation of 30 grams of dextrose yielded 119 c.c. of CO_2 in 24 hours. Under irradiation by ultraviolet the yield was 2743 c.c. of CO_2. Although exposure to ultraviolet rays in fermentation conditions favored the activity of the yeast, exposure of the cells in a shallow layer of liquid produced fatal results.[4]

[2] Much of this literature is disfigured by unhappy wording. Thus, we read of "objective pain," of "chemically pure" rays, and of the "solubility" of ultraviolet in protoplasm. One writer calls the direction of the ray which is normal to the tangential plane the "tangential" direction: it is of course, as far from being tangential as is physically possible. Examples of this kind as also of pseudo-mathematics, could be multiplied *ad nauseam*.

[3] Woch. Brau. 1922, *39*, 166; Chem. Abs. 1923, 17, 1686.

[4] See Söhngen and Coolhaas, Woch. Brau. 1923, *40*, 187; Chem. Abs. 1924, *18*, 1030; Rennhard, Compt. rend. Soc. Biol. 1923, *89*, 1080. The discordance is manifestly due to differences in experimental conditions.

This is a neat example of the two kinds of action, and it illustrates how they are, respectively, elicited. The rays of longer wave-length which suffer less absorption by air and by the liquid, are able to exert their stimulative action in appreciable depths. The rays of shorter wave-length are absorbed by the thinnest layers and in these, only, can their killing effect be exerted.

What are the mechanisms by which are effected the biologic actions of the ultraviolet rays? Little light has been thrown on this matter by the experimental results up to the present. For the most part these have been *ex post facto* laboratory confirmations of what may be called empirical field observations.

For these reasons, our citations, though we shall endeavor to maintain some semblance of order, cannot be expected to show much mutual coherence.

We have already learned that the ultraviolet component of solar radiation at the earth's surface is practically identical with the region which is possessed of stimulative action and which is not endowed with lethal power. In other words, living beings on the face of the earth have, at least partially, adapted themselves to exposure to rays of wave-lengths not shorter than 300 μμ (3000 Å). No natural occasion has arisen to evolve a mechanism protective against the shorter waves; these, therefore, preserve their fatal effect on living beings.

The fact that our protection against the solar ultraviolet is incomplete has led Woodruff [5] to suggest that our remote ancestors evolved in dark, cloudy regions, where such rays could reach the earth in only feeble amounts. The surmise may be correct, but it is at least as easy to suppose that the advantages of the stimulative action outweighed the relatively unimportant ill effects, and that excess of the latter was countered by the development of pigment.

Ultraviolet Absorptions of Eye Media.

As the sense organ of reception for solar radiation the retina would seem to require special protection. It is therefore not surprising that the structures of the eye through which the rays must pass in order to reach the retina act as filters of potentially injurious rays. Against natural ultraviolet the cornea affords little protection, as it is transparent to rays of wave-length greater than 295 μμ (2950 Å).[6]

It is the lens which is chiefly responsible for stopping ultraviolet rays from reaching the retina.

Chardonnet [7] used a quartz plate coated with a silver film of such a thickness as to be opaque to the visible and invisible spectrum except for the region between 301 μμ and 343 μμ. Through this plate normal eyes could not see an arc-light. But eyes from which the lens

[5] Tropical Light, 1916.

[6] Martin, Proc. Roy. Soc. 1912, *85*, 319. See also Schanz and Stockhausen, Arch. f. Ophth. 1908, *69*, 1. The vitreous and aqueous humors transmit the ultraviolet down to 300 μμ (3000 Å), Birsch-Hirschfeld, Arch. f. Ophth. 1909, *71*, 573. The effect of ultraviolet rays on the eye is discussed in Chapter 4.

[7] Compt. rend. 1883, 509.

had been removed (an operation performed for cataract) could detect the movement of the arc.

In addition to its absorptive power, the lens can arrest, or rather change, the rays by its peculiar property of fluorescence. The fluorescence of the lens is excited by rays between 350 μμ and 400 μμ (3500 and 4000 Å).

Thus we see that no radiation of wave-length shorter than 350 μμ (3500 Å) and probably than 380 μμ (3800 Å) can reach the retina. In the later period of life, owing to yellowing of the media, the limit is pushed into the most refrangible region of the visible spectrum.

Exposure of the eyes to ultraviolet rays does, however, result in inflammation, but only of the superficial structures. This effect is strictly comparable with the inflammations of the skin which are intentionally provoked as part of the routine of ultraviolet therapy. Like these, also, the conjunctival inflammations subside rapidly, without leaving any trace, on cessation of the exposure. It is rarely desirable to elicit such a reaction and in practice the eyes both of patient and operator are protected by bandages or glasses. (See Chapter 4.)

Verhoeff and Bell [8] have made elaborate studies of this subject. They conclude that the conjunctivitis is caused by the rays of wave-length shorter than 305 μμ (3050 Å). The action of rays of greater wave-length is balanced by processes of physiological repair.

Henri and Moycho [9] studied the effect of the ultraviolet spectrum on the skin of the rabbit's ear. Irritation was produced by rays from 330 μμ to 250 μμ (3300 to 2500 Å), with a maximum at 280 μμ (2800 Å).

Effect of the Ultraviolet on Proteins.

We noted in the preceding chapter the bare fact that the proteins are coagulated on exposure to ultraviolet radiation.

According to Mond [10] ultraviolet radiation increases the stability of colloidal condition of globulin and fibrinogen solutions, while the stability of albumin solutions is diminished. In the case of fibrinogen and globulin the coagulation temperature is raised; with albumin solutions the coagulation temperature is lowered, as are also the ammonium sulfate and the alcohol precipitation numbers. The reaction of serum-globulin and albumin solutions is rendered more acid, while the surface tension shows a decrease which is least in the case of albumin. Viscosity increases owing, probably, to the formation of aggregates. According to the same worker [11] the radiation of solutions of crystallized egg and serum albumins with ultraviolet rays at various hydrogen-ion concentration caused a shifting of the p_H towards the acid side in solutions with a $p_H < 4.6$, and toward the alkaline side in solutions of $p_H < 4.3$. Radiation of lecithin suspensions increased the acidity.

[8] Proc. Am. Acad. Arts Sci. 1916, *51*, 640.
[9] Compt. rend. 1914, *158*, 1509.
[10] Pflüger's Archiv 1922, *196*, 540; J. Chem. Soc. 1923, *123* and *124*, i, 868.
[11] Arch. ges. Physiol. Pflüger's, 1923, *200*, 374.

This work of Mond's recalls the observations of Burge [12] to the effect that the radiation changes cell protoplasm in such a manner that certain salts can combine with it and form a precipitate or coagulum. Burge found that abnormal quantities of calcium salts or of sodium silicate in the cells of the eyelids or of the cornea augmented the inflammatory action of the radiation. By exposing fish, living in dilute solutions of such salts, to ultraviolet rays he was able to produce cataract. Another aspect is dealt with in the work of Bovie and his collaborators.

The action of ultraviolet rays on living cells has been studied by Bovie [13] by its effect on certain constituents of protoplasm. Fresh egg albumin when exposed in a quartz tube at 10 centimeters from a quartz mercury vapor lamp at room temperature, began to show a feathery coagulum in 1 to 2 hours on the wall nearest the lamp, and after 35 hours was quite fully coagulated. The odor was peculiar and quite strong. When dissolved in water the same phenomenon was noticed, the time being shortened, possibly due to better penetration. The coagulated material settled to the bottom of the tube. A solution of egg albumin which has been crystallized and not freed from ammonium sulfate coagulated more rapidly than fresh egg white. Solutions of crystallized egg albumin from which the ammonium sulfate had been separated by dialysis was more sensitive, some being coagulated when exposed in glass tubes which cut off the shorter waves. Ox-serum is coagulated when exposed to ultraviolet radiation in quartz tubes, but not in glass. The coagulated material resembles the material coagulated by heat in that it is insoluble in alcohol, water and dilute acids, but is soluble in dilute alkalis.

The effect of temperature on this coagulation was also studied by Bovie.[14] When kept at 0° C. no coagulation occurred in a 5 per cent solution of crystallized egg albumin after 35 hours' exposure, but on warming a few degrees coagulation began, and tubes became turbid. If the temperature was again brought to 0° C. the tube cleared up, that is the reaction was reversed. This phenomenon occurred only when the temperature was reduced as soon as coagulation began. If a clear solution of the albumin which has been exposed to the light for some time at 0° C. is taken from the light and warmed, the coagulation occurs at about the same rate as though it was being exposed. It thus appears that the light produces some substance which causes coagulation, but that at 0° C. this substance is not capable of bringing about visible coagulation. Paramecium caudatum was exposed to the influence of ultraviolet radiation, the intensity of the radiation being such that an exposure of 8 seconds produced cytolysis in 57 per cent of the exposed organisms.[15] The organisms were given two exposures of 4 seconds each, separated by an interval of varying duration. An increase in the length of the interval be-

[12] Am. J. Physiol. 1916, *39*, 335.
[13] Science 1913, 24.
[14] Science 1913, 374.
[15] Bovie and Hughes, J. Gen. Physiology 1919, *1*, 323.

tween the two exposures resulted in a decrease in the percentage of cytolyzed paramecia. The percentage of cytolysis increased with the length of exposure; the curve being practically a straight line. Cytolysis occurs when a certain amount of a toxic photo-product is formed, and recovery depends upon the removal of this toxic substance. When paramecium caudatum was exposed to ultraviolet rays for four seconds at 17-18° death did not result, but subsequent heating for 60 seconds at 16-17° resulted in a 10 per cent mortality according to Bovie and Klein.[16] Heat alone at the same temperature and duration was not fatal. Heating at 24-26° for 60 seconds, then exposing to the radiation for 4 seconds gave an 8 per cent mortality, while subjection to the radiation followed by a temperature of 24-26° for 60 minutes caused a 66 per cent mortality. The percentage of recovery increased with the increase of the interval between radiation and subjection to temperature. With a period of one-half hour, the percentage of death was 20, while with a 5-hour period it was zero. The death of paramecium following ultraviolet radiation is a destruction by heat, the organism having been sensitized to heat in such a way that it can no longer endure normal optimum temperature. No theory of the action of rays can be complete which does not take heat sensitization into account.

Bovie returned to this work, in collaboration with Daland,[17] because the experiments just cited are open to criticism due to the spurious effects of the ozone generated by the ultraviolet rays to which the organisms were exposed. The experiments have been repeated under conditions which exclude the influence of ozone and the earlier conclusion is confirmed, viz., sub-lethal exposure to ultraviolet rays renders the organism (Paramecium caudatum) extremely sensitive to heat, so that it is injured and killed by an amount of heat which would not affect a normal unradiated individual. It is suggested that the uniqueness of the biological effects of radiation lies in the fact that the rays form within the cell chemical combinations which are foreign to normal protoplasm. The radiated organism which has not been exposed to an increased temperature may appear quite as normal as if the rays had no effect whatever. It is only when the initial photochemical change, "latent image," has been "developed" by the metabolic changes occurring at higher temperatures that the effects of the exposure are to be observed.[18]

Koertz[19] has studied the relation of the physico-chemical condition of cell colloids to their sensitiveness to irradiation. Suspensions (0.2-0.4 per cent) of corpuscles in isotonic salt solutions were subjected to irradiation by ultraviolet rays until lysis was initiated. The time for complete lysis (without further irradiation) was determined. The Hofmeister series held: The various anions and cations had the same effect as on lysis by hypotonicity, ethyl alcohol or heat. The

[16] J. Gen. Physiology 1919, *1*, 331.
[17] Am. J. Physiol. 1923, *66*, 55.
[18] Chem. Abs. 1923, *17*, 3512.
[19] Biochem. Z. 1923, *137*, 372; Chem. Abs. 1923, *17*, 3682.

effects of irradiation plus ethyl alcohol or hypotonicity are additive. Irradiation affects the cell protein rather than surface colloids. Whether the stroma or blood pigment is primarily concerned could not be determined but lysis and methemoglobin production are certainly not interdependent. These experiments show that the physicochemical condition of the cell protein influences sensitivity to irradiation, and also show the influence of the several ions on denaturized cell-protein.

The experiments of Clark [20] support the theory that the action of light on organic compounds is an emission of electrons from the substance affected, i.e., the ionization of photoelectric mols. Radiation of solutions of egg albumin by ultraviolet produces a greater aggregation when the albumin particles are negatively charged and a state of greater dispersion when they are uncharged or charged positively. In experiments by Howell,[21] the precipitation of fibrinogen brought about by ultraviolet rays was inhibited by the presence of hematoporphyrin. The effect of this sensitizer is to render the visible and ultraviolet rays capable of changing the fibrinogen into a more soluble form of protein. The fibrinogen which is insoluble in water is changed into a protein soluble in water, non-precipitable by heat and non-coagulable in its solutions by the action of thrombin. This modification is analogous to that produced by alkali.

According to Noack,[22] the chemical action of light on cells occurs through the agency of substances which transform light energy into chemical energy. Two groups of such catalysts are recognized: fluorescent organic compounds, and salts of certain heavy metals. Both serve as carriers of oxygen. From experiments on chromogens and many plants Noack concludes that the fluorescent organic compounds act by the formation of peroxides. Their action is stopped by sodium sulfite. The salts of the heavy metals act by change in the valence of the metal.

The observations of Schanz [23] on the lens of the eye have shown that the effect of light is to render protein less soluble. The presence of acetone in diabetes, coupled with the frequent occurrence of lenticular opacity, suggested a series of experiments in which equal amounts of a protein solution in a series of quartz tubes were treated with increasing amounts of acetone. Series one and two were placed in the sunshine, while series three was incubated in the dark at 38°. After four days the amount of precipitation was then noted in each case, the results showing that the change from a more or less soluble condition of the protein was due to the effect of light on the protein itself, the reaction, however, being increased by the presence of acetone. The action of ultraviolet rays on egg and serum proteins has been found by Schanz [24] to bring about a considerable degree of

[20] Am. J. Physiol. 1922, *61*, *72*; Chem. Abs. 1922, *16*, 2875.
[21] Arch. intern. physiol. 1921, *18*, 269; Chem. Abs. 1922, *16*, 935.
[22] Z. Botan. 1920, *12*, 273.
[23] Pflüger's Archiv 1918, *170*, 646; J. Chem. Soc. 1920, *118*, ii, 213.
[24] Arch. ges. Physiol. 1916, *164*, 445; Chem. Zentr. 1916, *87*, II, 670; Chem. Abs. 1916, 1656.

modification. In alkaline solution the amount of bodies precipitated by ammonium sulfate and sodium chloride was decreased, while in acid solution, the amount precipitated was increased. The change produced by light is regarded as a gelatinization of the proteins. This action is increased by the presence of oxygen. Kreibich [25] has found that ultraviolet rays render proteins insoluble. This, in the case of cells, causes catalase to become more firmly bound, retards catalase action, and results in pyknosis and hyaline degeneration.

Effects on Enzymes and the Like.

In view of the importance of enzyme action in biologic processes, the experiments of Pincussen and others on the action of ultraviolet light on enzymes are directly relevant to our present subject, though the ferments they dealt with were not those likely to be concerned in ultraviolet therapy.

Agulhon,[26] as the result of experiments on ferments with visible and invisible rays, *in vacuo* and in the presence of oxygen, divides enzymes into three classes according to their reactions:

I. Enzymes destroyed by all radiations, in the presence of oxygen: by ultraviolet, only, in vacuum: e.g., sucrase, tyrosinase, laccase.
II. Enzymes destroyed by all radiations, with or without oxygen: e.g., emulsin, catalase.
III. Enzymes destroyed in a vacuum by ultraviolet and somewhat weakened by visible rays: e.g., rennet.

Pincussen [27] reports that diastase, independently of dilution, loses its activity on exposure to ultraviolet rays in a quartz tube, but not in the sunlight. The destruction by light is greatest at p_H 4.6, which is the optimum reaction for diastatic activity, and is least between p_H 7 and 7.4. The presence of salts influences the destruction by ultraviolet light, iodide increasing it. Sugars cause little change in the amount of destruction, though in presence of dextrose even sunlight is slightly effective. The effect of ultraviolet radiation is inhibited by glycine and starch. Temperature has apparently little effect. Pincussen and di Renzo [28] state that the inactivation by ultraviolet rays of 0.1 per cent malt diastase acting on 1 per cent starch solution at varying p_H proceeds as a unimolecular reaction, while in the presence of 0.5 per cent of starch the later stages only correspond to the unimolecular equation. The departure from the simple equation is still more marked in the presence of 0.25 per cent of starch. A 0.2 per cent solution of the enzyme gives complex results in the presence of 1.0, 0.5, and 0.25 per cent starch solutions.

[25] Arch. Path. Anat. (Virchow's) 1916, *222*, 28; Chem. Abs. 1920, *14*, 2023.
[26] Compt. rend. 1911, *153*, 979.
[27] Biochem. Zeits. 1923, *134*, 459; J. S. C. I. 1923, *42*, 370 A.
[28] Biochem. Z. 1924, *144*, 366.

Continuing his researches into the physico-chemical conditions of the reactions between ultraviolet rays and the enzymes, Pincussen [29] finds that sodium chloride protects both the diastase and maltase in malt diastase from inactivation by exposure to sunlight. M/6-Phosphate solution protects malt diastase and the maltase of "pancreatin Rhenania" from inactivation by ultraviolet rays, while more dilute phosphate solutions are less effective. Similar results are given by acetate solutions of the same p_H. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at p_H 6.64. Ammonium, potassium, and lithium chlorides, potassium bromide, and sodium fluoride protect taka-diastase from ultraviolet rays to varying degrees, an effect which is more marked in dilute solutions of these salts than in more concentrated solutions. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures.

Pincussen [30] determined the action of malt diastase on soluble starch is inhibited, more especially in acid solution, by ultraviolet irradiation in the presence of potassium iodide. Under the same conditions, iodide has little influence on the enzyme in the dark. On the other hand, the actions of salivary and taka-diastases are increased by irradiation, especially in alkaline solution, while pancreatic diastases show a similar but very much less marked behavior. The results are correlated with a balance between the protective action of potassium iodide and the inhibitory action of iodine liberated from it by the ultraviolet irradiation.

The inhibitory action of ultraviolet irradiation on trypsin is maximal in the absence of iodides of the alkali or alkaline-earth metals. Little or no difference was detected in the influence of previously irradiated or non-irradiated salts on enzyme solutions kept in the dark.[31]

According to Pincussen and Kato,[32] sunlight acting on urease solutions at p_H 6.4 diminishes the activity both of the active constituent and of "Stable Component-X." Potassium hydrogen phosphate at p_H 5.6 affords a partial protection to the active component, but even in the dark the activity of the other constituent is decreased by phosphate. Ultraviolet radiation destroys the active enzyme both in the presence and absence of phosphate, but has not such a marked effect as sunlight in inhibiting Component-X.

Lüers and Lorinser [33] compared the heat inactivation of malt amylase with the effect on that ferment of ultraviolet radiation. The zone of maximal thermostability of malt amylase is displaced towards higher p_H values by increased concentration of an acetate buffer. Gelatin, egg albumin, and gum arabic protect the amylase from heat inactivation especially between p_H 6.0 and 7.0, and produce a flattening of

[29] Biochem. Z. 1924, *144*, 372.
[30] Biochem. Z. 1924, *152*, 406.
[31] Pincussen and Klissiunis, Biochem. Z. 1924, *152*, 416.
[32] Biochem. Z. 1923, *142*, 228.
[33] Biochem. Z. 1924, *144*, 212.

the zone of maximum stability. Maltose has a similar protective influence and a direct proportionality exists between log $C_{maltose}$ and the coefficient of inactivation. The inactivation of amylase by ultraviolet radiation follows neither the mono- or bi-molecular equation, nor the Schütz law. The effect of alterations in the hydrogen-ion concentration is much less marked in this case than in that of heat-inactivation. The temperature coefficient for ultraviolet inactivation is k^{30}/k^{20} 1.30, and physico-chemically the two methods of inactivation are dissimilar.

Effects on Antibodies etc.

It is probable that the relation of antibodies to ultraviolet therapy is closer than that of the enzymes. Heuer [34] reports that antibodies are sensitive to ultraviolet rays when diluted and are so in direct proportion to the amount of dilution. The agglutinins for cholera and paratyphoid A are less resistant to ultraviolet rays than those for typhoid. The bacteriolysins are less resistant than the agglutinins. This worker in collaboration with Potthoff [35] made experiments *in vivo* on the same subject. They found that the exposure of animals to ultraviolet rays has only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones. However, at the height of antibody formation, when the titer is somewhat constant, exposure of animals to ultraviolet rays causes a very great increase in the titer. This effect, however, is not permanent and the return of titer to preimmunization level is much more rapid than in the unexposed animals.

According to Fiedberger and Scimone,[36] on subjecting hemolytic serum to ultraviolet rays a decrease in amboceptor of the serum takes place. The albumin fraction is more resistant than the globulin. The end piece of complement is the more resistant. The lytic function of eel serum is more resistant than the toxic. Trypanosomes subjected to ultraviolet lose their infectivity much earlier than their motility. Wassermann serums and Sachs-Georgi positive serums of man and rabbits, on treatment with ultraviolet rays, become negative, especially if diluted and agitated. There is no influence on negative serums and extracts.

Albela,[37] working on rabbits intensively irradiated, for long periods, with the ultraviolet, was unable to detect any modification of the phagocytic action, as determined by the concentration of opsonins in the serum.

Effects on the Chemistry and Histology of the Blood.

The effects of radiation on the histologic and serologic characters of the blood have been examined by Koopman,[38] who reports that the

[34] Centr. Bakt. Parasitenk., I Abt. 1922, *88*, 380.
[35] Centr. Bakt. Parasitenk., I Abt. 1922, *88*, 299; Chem. Abs. 1923, *17*, 144.
[36] Z. Immunitäts. 1923, *37*, 341; Chem. Abs. 1924, 551.
[37] Deut. Med. Wochschr. 1922, *48*, 1347.
[38] Deut. Med. Wochschr. 1924, *50*, 277. If leucocytes are radiated upon with

effect of ultraviolet rays was investigated on eight persons, five of whom were normal. The concentration of erythrocytes is not changed. The leucocyte count increases the first hour, then decreases and is still low after 6 hours' irradiation. The neutrophile count may be increased during the first 3 hours. The lymphocyte count is increased. Hemoglobin, viscosity and coagulation point are unchanged. A guinea pig was irradiated for 1 to 3 hours, 80 cm. from the lamp. The complement concentration was doubled during the first hour but was markedly decreased during the subsequent 2 hours. A 3 hour exposure led, regularly, to the death of the pig. The blood was free from complement. The irradiation of cooled guinea pig serum, *in vitro*, leads to inactivation of the complement.

According to Clark [39] the effect of the radiation depends on the wave-length. Thus radiation with rays of 400 μμ to 300 μμ (4000 Å to 3000 Å) causes leucopenia (reduction in the number of white corpuscles), while rays of 300 μμ to 200 μμ (3000 Å to 2000 Å) produce lymphocytosis (increase of the white corpuscles of lymphatic origin).

Kroetz [40] reports that in most patients, the water content of the serum increases after irradiation with ultraviolet or X-rays, but is again normal after 24 hours. The alteration of ionic equilibrium in the serum of the irradiated individual is summarized as an increase in the ratio $K^{\cdot} \times (H_2PO'_4 + HPO''_4)/Ca^{\cdot\cdot}$. Refractometric measurements reveal an alteration in the serum proteins after treatment.

According to Balderrey and Barkus [41] exposure of the human body to radiations of light energy (sunlight) increases the alkalinity of the blood. The degree of pigmentation present has a direct influence on the change in the reaction of blood. The greater the amount of pigmentation the more marked the change in the p_H of the blood. Considering that the determinations as to the hydrogen ion concentration of the blood, before and after radiation, were made with light rich in the longer wave-lengths and when the extremely short wave-lengths were at a minimum, in all probability the wave-lengths most active in this reaction of the body to radiation are those of the visible spectrum. Variations in the intensity of light, as evidenced by continuous bright sunlight, increased temperature and lessened humidity, materially influence the effect of light upon the reaction of the blood.

Frenkel-Tissot [42] has found that healthy people in the mountains show the same blood sugar figures as on the plains. In internal and in

ordinary light the granules containing oxidase disappear only if the temperature rises above 62°; by radiating with ultraviolet they disappear without a rise of temperature. Vedder, Nederland, Tijdschr. Geneeskunde 1924, *68*, 2357. Shamberg and Brown, Arch. Intern. Med. 1925, *35*, 537, find that exposure of rabbits to ultraviolet decreases the concentration of lipase and increases that of the protease of the blood but decreases the concentration of both in the skin. Jaulmes, Compt rend. soc. biol. 1925, *92*, 268, could discern no effect upon the blood with respect to its cellular composition on exposure to a Wood light (a mercury vapor lamp equipped with Wood's screens).

[39] Cited by Pacini, Outline of Ultraviolet Therapy, 1923, 36.

[40] Biochem. Z. 1924, *151*, 449.

[41] Am. Rev. Tuberculoses 1924, *9*, 107.

[42] Deut. Arch. klin. Med. 1920, *133*, 286; Chem. Abs. 1921, *15*, 118.

surgical diseases, the blood sugar is the same as in patients with the same diseases on the plains. However, in normal people on the mountains, sunning, raying with the quartz-lamp, and hyperthermia have a very different action. Those with a high blood sugar value show a tendency for this to be lowered by these effects, while those with normal or low values have a tendency towards an increase.

Influence of Dyestuffs and "Sensitizers."

According to Eckstein and v. Möllendorff [43] animals exposed to ultraviolet rays, after injection of dyes, and killed 1 hour later, showed accumulation of the dyes in the kidneys, while irradiated controls showed none. When the animals were killed after a longer interval, dye deposits were found in the kidneys both of the radiated and of the control animals, and in larger quantities in the latter. Prolongation of the radiation produced degeneration of the dyed tubules. Such typical findings were observed only in the kidneys. These findings are recorded here for reference without any explanations. The conditions are far too complex to admit of ready analysis.

This is less the case with experiments on animals which have received a preliminary dose of quinine or quinidine (dextro-quinine). The optical properties of these alkaloids are such as to class them among drugs likely to produce sensitization, or, at any rate, a variation from the normal reaction. Macht and Teagarden [44] found that the pharmacologic activity of the sulfates of these alkaloids was enhanced by exposure of the animals to light, especially to ultraviolet radiation (Alpine "Sun Lamp"). The absolute lethal dose was smaller for the animals kept in the light than for those in the dark. The laevo-variety (quinine) was more toxic than quinidine.

In the same line are the experiments of Azzi.[45] Subcutaneous injections of 0.005 g. quinine hydrochloride per kg. and over cause a marked leucocytosis at sea-level both in animals kept in the dark and in those with shaven backs exposed to diffuse light. At high altitudes doses as low as 0.0025 g. per kg., followed by exposure to diffuse light, caused an increase. At sea level and in the dark on the mountain top doses of 0.005 g. per kg. and over diminished the phagocytosis of tubercle bacilli killed by heating 1 hour at 90°, while in the animals exposed to the light on the mountain top a dose of 0.005 g. per kg. decreased, and a dose of 0.0025 g. increased the phagocytosis. This action is ascribed to the ultraviolet rays at high altitudes.

Schanz [46] has suggested, with some plausibility, that one of the rôles of chlorophyll is that of a sensitizer for the associated protein.

[43] Arch. Kinderheilk. 1923, *62*, 206; Chem. Abs. 1923, *17*, 3718.
[44] J. Pharmacol. 1923, *22*, 21.
[45] Arch. sci. med. 1922, *45*, 212; Chem. Abs. 1923, *17*, 3541.
[46] Biol. Zentr. Berlin 1919; Pflüger's Arch. *170*. Schanz, Ber. botan. Ges. 1923, *41*, 165; Chem. Abs. 1923, *17*, 3040, observes that the toxic effects of ultraviolet upon plant plasma are realized at longer wave-lengths in the presence of sensitizers. Erythrosin and eosin are not poisonous to the plant in the dark but cause death in the light. Methylene blue is not toxic.

The latter, alone, is sensitive only to ultraviolet rays of the shorter wave-lengths. In combination with chlorophyll, according to Schanz, it becomes sensitive to and able to utilize the rays of the visible spectrum. His evidence in support is based on experiments with plants grown (1) in the open air, (2) under Euphos glass which absorbs all ultraviolet and some violet and blue rays, (3) under ordinary glass. The plants in experiment (2) grew largest, but seemed somewhat etiolated; those in (3) were next largest; those in (1) were normal and less free growing. In these experiments precautions were taken to ensure due ventilation.

The protection against the action of ultraviolet rays afforded to alexin and sensitizer by certain substances, has been investigated by Hill and Schmidt,[47] who state that although the unit of sensitizer is more easily destroyed by exposure to ultraviolet rays than the unit of alexin, the difference is not real, since the concentration of serum proteins is enormously different. In dilutions more nearly comparable alexin is more quickly destroyed than the sensitizer. The aromatic amino acids, tyrosine and phenylalanine, proteins containing these amino acids and certain substances belonging to the aromatic series show marked protective action for alexin and the sensitizer against the action of ultraviolet rays. Since destruction cannot take place without absorption it is possible that the difference in susceptibility shown by alexin and sensitizer toward ultraviolet is due to a difference in aromatic amino-acid content.

The Influence of Radiation on Metabolism.

Pincussen and Floros[48] by experiments *in vitro* attempted to obtain information as to the fate of nucleins exposed to radiation. Specimens of nucleic acid were exposed to the rays of a nitral lamp of 300 N.K. Heat rays were absorbed by water. The effect was determined by changes in specific rotation of the solution of nucleic acid as such or sensitized with eosin or dichloroanthracene. The splitting was pronounced in the presence of eosin and the substance alone, but not noticeable with the anthracene compound. Studies of the effect of these factors on the splitting of nucleic acid by blood serum showed that enzyme activity is not increased. Other investigations demonstrated that light radiation causes a further oxidation of the purine bases, particularly uric acid. In these conditions the main oxidation decomposition product of the purine bases, e.g., uric acid, is oxalic acid.

Ederer[49] studied the action of artificial light on alveolar carbon

[47] J. Infect. Dis. 1919, *25*, 335; Chem. Abs. 1919, 3234.
[48] Biochem. Z. 1921, *126*, 86; Chem. Abs. 1922, *16*, 1608.
[49] Biochem. Z. 1922, *132*, 103; Chem. Abs. 1923, *17*, 303. Interesting results reported by Saidman (Compt. rend. 1925, *180*, 693) concerning the photoelectric effects of ultraviolet rays on the human body require further study. Saidman observed that there exists in the normal man a dissipation of negative electricity under daylight. If the subject is illuminated with a 2000 candle power lamp of white light the dissipation is not sensibly increased. If the person is subjected to the action of ultraviolet rays, a rapid discharge is produced. Accordingly there exists in man a true photoelectric effect.

dioxide tensions. Radiation of man by means of a quartz lamp produces different effects on the carbon dioxide tension of alveolar air according to the strength of the dosage administered. Weak stimulation has no effect; radiation of medium intensity increases the tension and strong radiation leads to a lowering. The action of this type of artificial illumination on the carbon dioxide tension is independent of the erythema of the skin. The hypercapnic effect is not of central origin, for the organism as a whole becomes over-sensitive, but is probably hematogenous. This interpretation is based on a probable increase in the alkalinity of the blood, a decrease in the acid products of metabolism and a change in the colloid state of the blood proteins.

Pincussen [50] investigated the effect of solar radiation on the protein metabolism of rabbits. He notes a stimulation of the general metabolism as shown by an increase in nitrogenous excretion. Sensitizers, such as various dyestuffs and potassium iodide, still further increase the nitrogen excretion. Differences in the action of the various sensitizers may be observed in their effect on individual constituents of the total excreted nitrogen.[51]

On the other hand Liebesny [52] fed two dogs on a constant diet of horse tripe and found that exposure to the ultraviolet rays from a mercury vapor lamp caused an appreciable reduction in the volume of urine and in its total nitrogen, creatinine, and neutral sulfur content.

Ultraviolet Radiation and Avitaminosis.

Certainly the most sensational and, probably, the most important discoveries, in connection with the influence on metabolism of ultraviolet radiation, are those announced in recent years from laboratories and hospitals concerning the effect of the radiation in curing and preventing certain deficiency diseases, notably rickets. It might seem logical to deal here with the experimental side of this important question. In view, however, of the essential unity of the whole matter, and of the interwoven relations of the laboratory and the clinical aspects, it has seemed better to consider the entire subject in a special section of the therapeutic part of this chapter.

Miscellaneous Effects.

Henri and (Mme.) Henri [53] have shown that ultraviolet rays produce involuntary movements in small animals, that a fixed minimum exposure (initial period) is required to produce this effect, and that a definite time (latent period) elapses between the termination of the initial period and the movement. Experiments were carried out to determine what processes occur during the initial period. The results show that during the initial period photochemical reactions take place

[50] Biochem. Z. 1924, *150*, 36.

[51] In connection with this question of sensitization, see also the preceding chapter, p. 244, and this chapter, p. 281.

[52] Z. physik. diätet. Therap. 1920, *24*, 182.

[53] Compt. rend. 1912, *155*, 414; J. Chem. Soc. 1912, 102, ii, 964.

in the peripheral organs, and that the products of these reactions are distributed by diffusion and osmosis. The initial and latent periods are not affected by change of temperature. Prolonged exposure to ultraviolet rays renders Cyclops immobile but it responds to ultraviolet rays, and the "initial period" is then longer, but gradually returns to its primitive value. This is also the case with an animal in which the nerve terminals have been anæsthetized by ether. The phenomena of fatigue and recovery of excitability by ultraviolet radiation, therefore, have their seat in the peripheral organs.

Lord Avebury [54] refers to the range of frequency of light-vibrations visible to bees. These insects apparently distinguish color, though the range of color that appeals to them may be different from that recognized by us. There is no reason to believe from that, that ultraviolet rays, which could not be detected in the form of light by the human eye, are invisible to bees.

Baldwin [55] in an investigation of the nature and mechanism of causation of certain abnormal developmental results, obtained by exposure of restricted areas of the fertilized ovum of the frog to ultraviolet rays, states that it does not appear reasonable to infer that one or all of the corresponding groups of substances may be susceptible to the influence of the rays while still in the living ovum. Exovation, as the direct result of the application of a great amount of energy, may be cited as an instance of the alteration. The normal histological features of the embryo, and of the adult tadpoles, however, argue the presence of a process of reversal, during the time of development of the embryo, of the changes which were brought about through the activity of the rays.

Secerov [56] exposed a white-haired guinea pig and rabbit to the action of ultraviolet rays for a considerable time. In the case of the guinea pig the hair became yellow after from 35 to 40 hours and that of the rabbit after 80 hours finally became reddish yellow. With animals partly black and partly white the coloration of white hairs takes place more rapidly than with a pure white animal. This coloration of the hair takes place when the hair is removed from the animal but not so rapidly as when attached.

Lillie and Baskerville [57] reporting experiments on starfish eggs state that the effects produced in unfertilized eggs by brief radiation with ultraviolet rays resemble those of partial activation. The immediate change produced in the egg system is of the same essential nature as that caused by temporary exposure to high temperature or other activating agent. The primary effect of the rays is probably a structural change, i.e., a change in the colloidal substratum of the protoplasm and probably of the surface layer, upon which follow specific chemical effects as a secondary consequence.

The fluorescence and inhibition of luminescence in ctenophores by

[54] Illuminating Engineer, London, 1908, 1, 689.
[55] Biol. Bull. 1919, *37*, 294; Chem. Abs. 1920, *14*, 1164.
[56] Compt. rend. 1914, *158*, 1826.
[57] Am. J. Physiol. 1922, *61*, 57; Chem. Abs. 1922, *16*, 2937.

ultraviolet rays is the subject of an investigation by Harvey.[58] Mechanical stimulation of luminescence in Mnemiopsis probably occurs chiefly through a nervous mechanism. Luminous tissue loses its power to luminesce in daylight and regains it, at least partially, in the dark. Luminescence of the entire animal or of the individual cells is suppressed by the near ultraviolet. This inhibition is not due to a stimulation through which the photogenic material is consumed. When animals are stimulated mechanically several times and placed in ultraviolet rays a luminescence appears as in mechanical stimulation. This luminescence is not obtained in light-adapted ctenophores. It is interpreted as a fluorescence of the oxidation of photogenic material. Such fluorescence may also be observed in ultraviolet rays in Photuris and Chætopterus, but not in Cypridina.

Bretin and Leulier[59] examined various drugs of vegetable origin to determine if fluorescence would serve as a means of identification. A mercury vapor arc lamp in argon was the source of light; the light was filtered through two Pyrex nickel glass plates. Most of the drugs gave a characteristic fluorescence.

The effect of ultraviolet rays on the germination and early growth of plants constitutes the basis of a protracted study by Popp.[60] For the seeds tested the following generalizations were found to hold:

1. Exposures of dry seeds to the full ultraviolet of a quartz mercury vapor arc have little or no effect on later germination and growth, even after 188 hours exposure. This may be due to inability of the short rays to penetrate the dry seed coats.

2. Exposures of less than 2 hours duration on soaked seeds that have not yet begun to sprout do not have a marked effect on germination. Probably here again there is not enough penetration of the short rays in so short a time, to cause any permanent injury.

3. Longer exposures to the open arc decrease the rate and the amount of germination, inhibit growth and development and finally cause death of the plants. The wave-lengths below 300 μμ are more effective in this respect than are those above 300 μμ.

4. In general cotyledons of seeds exposed to ultraviolet seem to have difficulty in emerging from the seed coats, but if they get through, they are not seriously injured by the short rays until after long exposures (120 hours).

5. Chlorophyll appears in the cotyledons of seedlings raised under the open arc about as rapidly as it does in ordinary light but never reaches the intensity it does in daylight.

6. Ultraviolet radiation does not seem to be necessary for the development of the reddish-purple pigment on the under side of the cotyledons of mustard. Under Noviol glass, which screens off all ultraviolet, and in the dark this pigment always appeared. It reached its deepest intensity uniformly in the greenhouse plants where comparatively little ultraviolet was present.

7. Geranium plants exposed to the open arc for 6 hours, after being in the dark 24 hours showed no difference in appearance at the end of the 6 hours, but tests of the leaves for starch at this time were entirely negative, while in ordinary light starch can be located in these leaves in an hour or less.

[58] J. Gen. Physiol. 1925, *7*, 331; cf. Chem. Abs. *19*, 862.

[59] Bull. sci. pharmacol. 1924, *31*, 630; cf. Bayle and Fabre, Chem. Abs. 1924, *18*, 1434, 3143.

[60] Private communication from Prof. H. W. Popp representing tentative conclusions from work conducted by him at Pennsylvania State College and at the Boyce Thompson Institute for Plant Research.

8. In no case were new leaves formed in mustard under ultraviolet rays. New leaves were formed in sunflower, Canada field peas, oats and corn, but these leaves were all killed in a day or two after they were formed.

9. A few plants were able to grow under the open arc in all of the series, but in no case was there any further development than would result from the food stored in the seeds.

10. Seedlings that do not survive the open arc will live longer under its rays than those grown in the dark at the same time. Since there is apparently very little food synthesis this may be due to a retarding of enzyme action or other germination processes. If these seedlings, after being exposed 6 to 8 hours a day for 10 to 15 days, are removed to the greenhouse, they immediately start to develop normally, but exposed seeds that have not germinated under ultraviolet rays cannot be made to germinate this way later.

11. Seedlings grown in daylight in the absence of ultraviolet or in complete darkness and then exposed to the open arc, are killed after 6 to 20 hours exposure. Similarly, the leaves of mature plants of geranium and coleus with 6 hours exposure to the open arc will have a burnt appearance the next day and fall off. In the seedlings the young leaves are most susceptible to injury and next the stems. Apparently those grown under the arc from the start are able to adapt themselves to it to a certain extent. Finally, of course, they too are killed.

12. When all ultraviolet was screened off, mustard seeds in visible light gave as high a rate and amount of germination as they did in complete darkness. This same effect was produced, however, when the seeds were exposed to all the rays between 600 and 300 μμ. If the ultraviolet between wave-lengths 400 and 300 μμ was the only radiation falling on the seeds, a somewhat lower rate and final amount of germination was observed. Apparently the inimical effects of the region between 400 and 300 μμ are overcome when visible light is falling on the plants at the same time.

13. No striking differences in growth and development of seedlings of mustard was observed when all ultraviolet was screened off as compared with seedlings grown under the rays between 600 and 300 μμ. If, however, the region between 400 and 300 μμ was the only one to which the seedlings were exposed, a distinct retarding of growth and development occurred.

14. Bacteria and general damping-off fungi do not develop in the rays of the open arc, but will if the region below 300 μμ is screened off.

To determine the effect of light of known wave-lengths and intensity on the growth of various kinds of plants, including tomato, buckwheat, petunia, sudan grass, soy beans, tobacco, 4 o'clocks, and sunflower experiments were conducted in five specially constructed greenhouses in which all conditions were kept practically the same except the quality of light falling on the plants. House 1 was covered with ordinary greenhouse glass and was used as a control; House 2 was covered with a clear glass (Corning G 86 B) which transmits the entire sun's spectrum and has a high percentage transmission of the blue-violet end of the spectrum; this house was shaded with tobacco shading cloth on the inside so as to reduce the light intensity to that of the houses having a limited spectrum (Houses 4 and 5); House 3 was covered with a lemon-yellow glass (Corning "Noviol O") which removed the ultraviolet part of sunlight; House 4, also covered with a yellow glass (Corning "Noviol C") cut out all of the ultraviolet, and violet and half of the blue of the sun's spectrum; the glass over House 5 (Corning "G 34") was orange-yellow in color and eliminated all ultraviolet, violet and blue and half of the green.

Besides general observations on vegetation, flowering and fruiting, macrochemical, microchemical and anatomical changes have been followed in some cases. From results so far obtained, the following has been found to hold for the plants experimented with:

I. When plants were grown in sunlight from which all wave-lengths below 529 μμ were eliminated, i.e., when only the red, orange and yellow and part of the green of the sun's spectrum reached the plants, they developed the following characteristics.

1. An increased rate of elongation of the main axis and usually a greater total length, with a reduction in the number of side-shoots or branches formed.
2. A considerable decrease in thickness of stem.
3. A general curling or rolling of leaves.
4. Good development of chlorophyll, as indicated by appearance in comparison with controls in full sunlight.
5. Less differentiation of stem and leaf tissues, less compact and thinner-walled cells, and a reduction in strengthening tissue.
6. Considerable delay in flowering and a reduction in the number of flowers produced.
7. Very weak fruiting and poor development of storage organs.
8. Decrease in fresh weight and dry weight and increase in percentage of moisture.
9. Considerable decrease in total carbohydrates and starch.
10. Decrease in some of the higher organic compounds and an increase in soluble nitrogen compounds.

The degree to which these different effects were produced varied with different species.

II. When all wave lengths below 472 μμ were removed, i.e., when the plants were grown in red, orange, yellow and green and part of the blue of sunlight, similar results were obtained but to a lesser degree.

III. When only the ultraviolet part of sunlight was removed, none of the above results were obtained with any of the plants used, although there was a small increase in length of stems in some cases. Some of the plants (tomato, petunia, sudan grass and sunflower) bloomed earlier when the ultraviolet was removed than they did under any other conditions. In general, these plants were little different from the controls in full sunlight.

IV. Some of these stated effects are similar to those obtained when, plants are grown under greatly reduced light intensities. That light intensity was not the important factor in these experiments is indicated by the fact that normal growth was obtained when the plants received the full sun's spectrum at an intensity that was at all times lower than that of the house in which all ultraviolet, violet and part of the blue was removed, and only slightly greater than that of the house which eliminated all rays down to the green.

V. The experiments as a whole indicate that the blue-violet end of the spectrum is necessary for normal, vigorous growth of plants, and in general that quality (or wave-length) of light is of considerable importance in all experiments dealing with the effect of light on plants.

Chapter 14.

Therapeutic Applications.

Finsen attributed his success in the light treatment of certain local affections to the action of the ultraviolet. But the radiation from the arc lamp used by Finsen was relatively poor in ultraviolet rays. Consequently the treatments were much prolonged and small areas only could be treated at one sitting.

The therapeutic quartz lamp[1] was used at first almost exclusively in surgery and in skin diseases; that is, local affections, in the manner employed by Finsen. Later, after improvements by Kromayer, it became most useful in this field.

The use of ultraviolet radiation in general diseases is a more recent development.

Rollier and others found that sun baths, especially at great altitudes, such as in the Alps, were beneficial in the treatment of tuberculosis (especially of the bones and the joints). These results were attributed to an abundance of ultraviolet rays in the sun's rays at these altitudes. As the ultraviolet rays of sunlight are largely absorbed in passage through the atmosphere, the value of ultraviolet rays in the sun bath treatment was long doubted. In fact, in 1903, Rieder made the assertion that the infra-red heat ray was the controlling factor in the beneficial effects of the sun bath.

The quartz lamp has afforded a means of studying the effects of ultraviolet rays upon the human body in general treatment, with the result that the preponderant rôle of the ultraviolet is now well established and its therapeutic application is constantly expanding.

Apparatus. (See Chap. 3.)

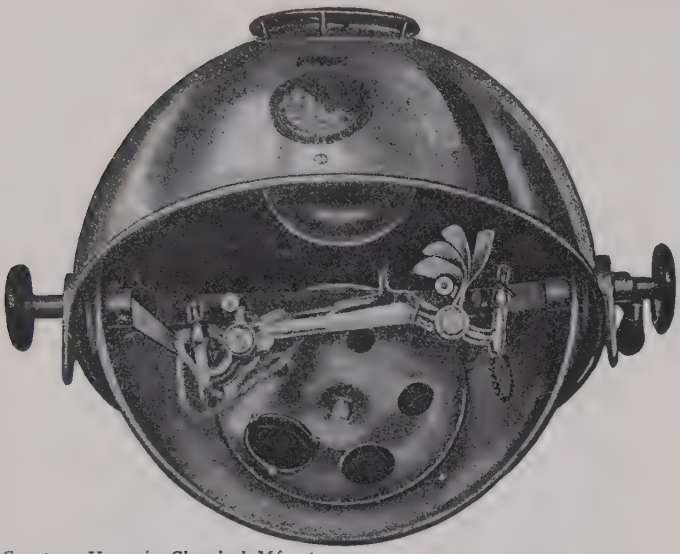
The types of quartz lamps suitable for therapeutic use have been described, together with the method of operation and illustrative cases, by Bach.[2]

Two types of lamp are used in the treatment of diseases, the air-cooled "sun-lamp" for general application or for the treatment of large areas and the water-cooled apparatus for local applications.

One type of air-cooled lamp consists of a quartz burner from two

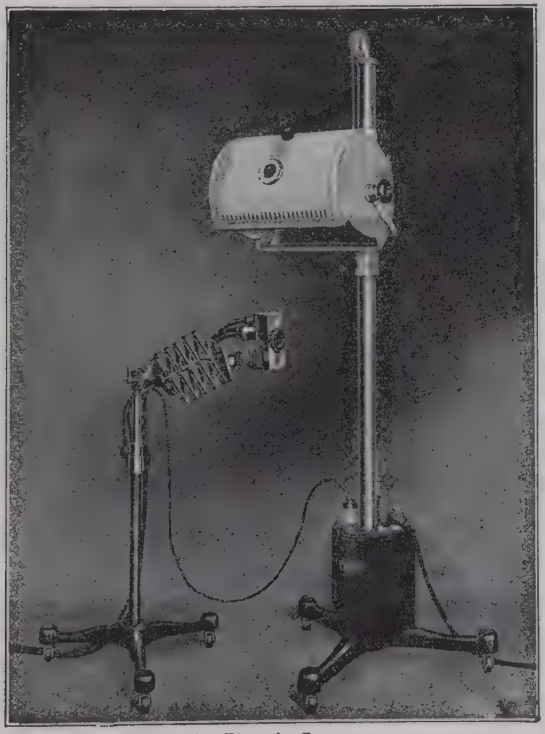
[1] Introduced in 1907 by the Quartzlampen Gesellschaft of Hanau, Germany, now made in the United States by the Hanovia Chemical and Manufacturing Co., Newark, New Jersey; by Victor X-ray Corporation, Chicago, Illinois, and by Burdick Cabinet Co., Milton, Wisconsin.

[2] Ultraviolet Light, New York, 1916; also Pacini, *Outline of Ultraviolet Therapy*, Chicago, Ill., 1923.



Courtesy Hanovia Chemical Mfg. Co.

FIG. 68a.—Hanovia (Air-Cooled) Lamp in Aluminum Hood.



Courtesy Cooper-Hewitt Electric Co.

FIG. 69.

and ½ to 5 inches in length, mounted in an aluminum reflector, which in some cases is fitted with a shutter by means of which the area of the surface to be exposed to the ultraviolet rays may be controlled. On one end or on both ends, as the case may be, the lamp

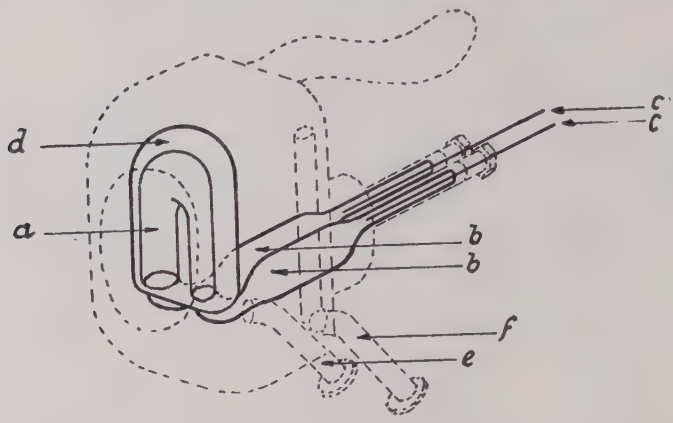
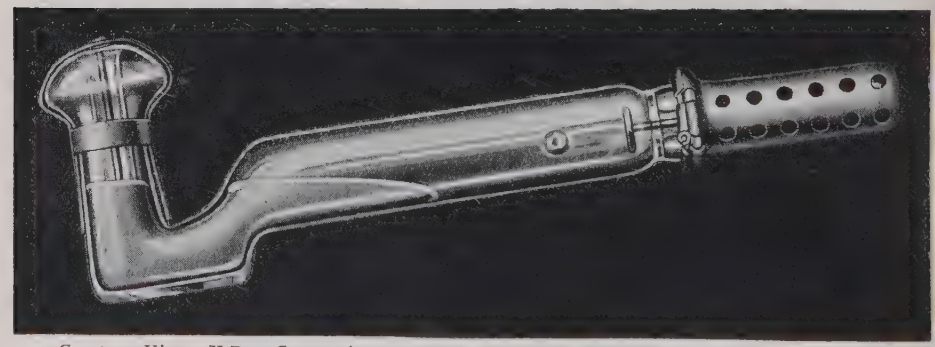


FIG. 70.—Kromayer Lamp.

is fitted with strips of metal which spread out fan-like, to serve as heat radiators thus to control the temperature of the lamp. Figure 68a. The burner and reflector are adjustably mounted either on a stand or rope support. A rheostat forms a part of the equipment. The burners are made for 90-120 volts and 200-240 volts direct current. In case



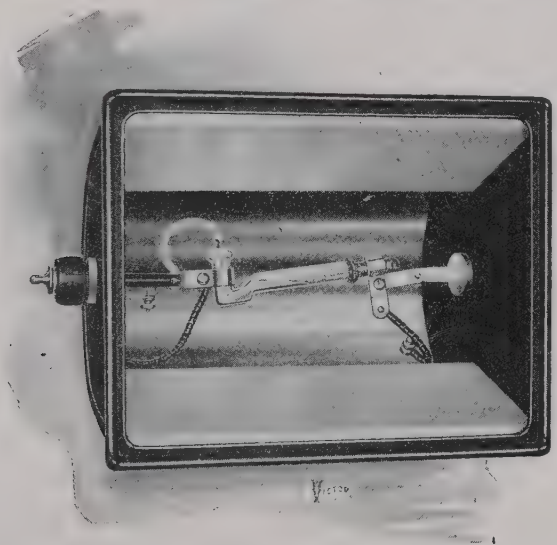
Courtesy Victor X-Ray Corporation.

FIG. 71.—Air-Cooled Type "Uviarc" Quartz Tube.

alternating current only is available a current rectifier or a motor generator set may be used. A form of lamp used by physicians is shown in Figure 69. A modification of the "sun-lamp" is equipped with a ring of incandescent lamps surrounding the reflector of the mercury

vapor lamp. These radiate heat and tend to counteract the coldness experienced by some persons during treatment, especially when protracted. There is also induced a hyperemia of the skin which is, sometimes, desirable. The effect of this form of treatment is more like that of a natural sun bath.

The Kromayer lamp is water-cooled and is typical of the class. It consists of a Ω-shaped tube of transparent fused rock crystal quartz. This tube is about ¼ inch internal diameter, and forms the arc tube "a." It carries on the ends two mercury containers "bb" at right angles to the plane of the arc tube, and these constitute the electrode vessels to



Courtesy Victor X-Ray Corporation.

FIG. 72.—Air-Cooled Lamp. Interior View of Rotary Casing. By pressing the knob on the left (exterior of hood) the mercury is made to flow toward the anode, thus completing the circuit and causing an electric arc.

which the current is conducted by ground-in mercury-sealed rods "cc." The arc is struck between the mercury poles and fills the whole length of the arc tube. In order to carry off the heat produced by the arc, when burning, the lamp is cooled by a supply of running water. The water must not, however, come in contact with the arc tube itself, as the resulting cooling of the arc would reduce the therapeutic effectiveness of the lamp and, for this reason, the arc tube is surrounded by an evacuated quartz jacket "d." The burner is built into a water-tight metal casing and emits its rays through a quartz window in the front of same. The cooling water circulates between the lamp and the metal body, the tube "e" forming the inlet and "f" the outlet. The rate of flow must be so regulated that the lamp body does not become heated.

In some forms of quartz lamp a tungsten anode is employed. The

makers claim for this that it simplifies construction and enables higher temperatures to be reached, giving greater intensity of radiation.

In the "Uviarc" tubes a graduated glass seal is used. This does away with the necessity for radiating fins to protect joints from overheating.

So far we have spoken, in this section, of the air-cooled and the water-cooled lamps as though the only difference between them was

Courtesy Victor X-Ray Corporation.

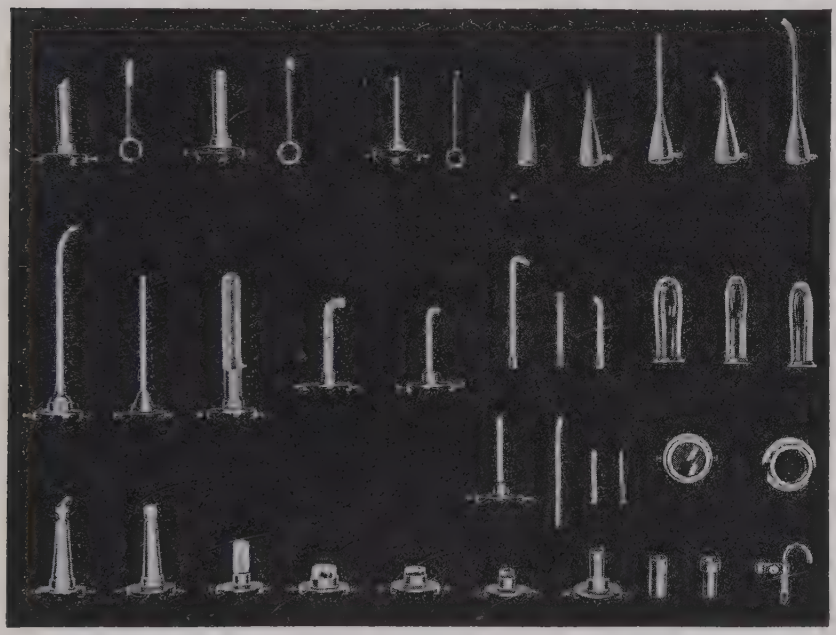
FIG. 73.—Water-Cooled Type.

that one (the air-cooled) was more convenient for general and the other (the water-cooled) for local intensive radiation ("focal radiation"). But Pacini (loc. cit. passim), following Wood, emphasizes a fundamental distinction between the radiations furnished by the two kinds of lamps. The air-cooled lamp is especially adapted to yield a radiation containing a larger proportion of the ultraviolet rays of wave lengths exceeding 300 μμ, i.e., rays possessed of what Pacini calls "biologic" effect, which we prefer to term "stimulative." [3]

[3] For the explanation see preceding chapter.

The water-cooled lamp, on the other hand, gives out an intense radiation, much of the energy of which is in the form of rays of wave lengths less than μμ 300. This region is endowed, as we have learned with lethal, or as Pacini calls it "abiotic" action.

Such of these lethal rays as are emitted from the air-cooled lamp can be absorbed by the air between the lamp and the object being irradiated. Therefore, when it is desired to elicit, in pure form, the stimulating action of the air-cooled lamp a considerable distance (e.g., about 40 inches) is allowed between the lamp and the patient.



Courtesy Hanovia Chemical Mfg. Co.

FIG. 74.

The characteristic lethal, or caustic, or "abiotic" action of the water-cooled lamp is obtained by the use of short lamp-to-patient distances.

In some instances this distance cannot directly be made short enough; e.g., in the natural body orifices, or in sinuses. Fortunately, an interesting property of transparent quartz comes to our aid in such a case. If ultraviolet rays are applied axially to a rod of quartz they pass along it, and are delivered at the other extremity with little diminution of intensity and this whatever the shape of the rod. It is as though the limiting surface between quartz and air were a surface of total (internal) reflection.

Taking advantage of this property applications are made of transparent quartz rod, of diverse forms, to adapt them for use in special positions. Some of the more usual shapes are illustrated in Figure 74.

To secure more effective action optical sensitizers may be applied to the surface to be rayed. These sensitizers may be weak solutions of suitable dyestuffs, such as eosin. Calcium chloride in aqueous solution may be used.

When the direction of the central ray is otherwise than normal to the surface ("tangential" direction of Pacini), it is evident that an allowance must be made for the resulting diminution in the intensity per unit area. Quantitatively this allowance is calculated by the well known cosine law: "The energy impinging on a unit surface varies

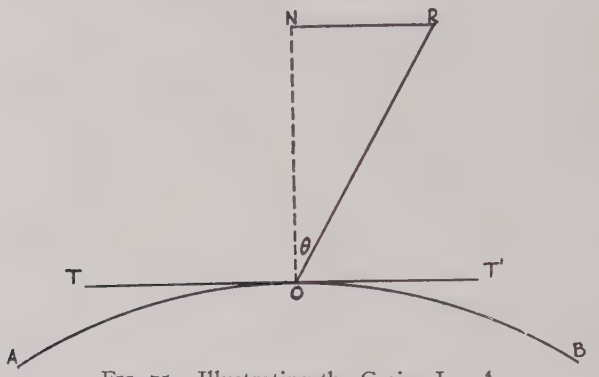


FIG. 75.—Illustrating the Cosine Law.[4]

directly as the cosine of the angle of incidence." The angle of incidence is the angle which the ray makes with the normal to the tangential plane. When the ray impinges normally to the surface the angle of incidence is 0°. The cosine of 0° = 1. When the ray impinges at an angle of 60° to the tangential plane, the angle of incidence = 30°, and the cosine of 30° = .87, i.e., the diminution of the intensity per unit area is, roughly, one-eighth.

In the following table the fourth column gives the factor by which the time of exposure determined for a normal ray must be multiplied to give approximately an equivalent exposure with oblique rays.

Angle Between Ray and Tangent Plane	Angle of Incidence Θ	Cosine Θ	Factor
90°	0°	1.000	x 0.00
75°	15°	0.966	x 1.03
60°	30°	0.866	x 1.16
50°	40°	0.766	x 1.30
45°	45°	0.707	x 1.40
30°	60°	0.500	x 2.00

This very elementary matter has been treated in detail because the account in some of the books on ultraviolet therapy is misleading or obscure.

[4] AOB = the recipient surface. TOT' = tangent.
NO = normal to TOT' and AOB.
RO = impinging ray.
Θ = angle of incidence. $\frac{ON}{OR}$ = cosine Θ.

The dosage has not yet come to be predetermined by any instrumental method. Reliance is placed first on experience with the particular type of patient and of radiation to enable a test exposure to be made. After this the dosage is determined according to the reactivity of the patient and the degree of reaction desired.

This book is not intended as a guide to the practitioner of ultraviolet therapy. It would, therefore, be out of place to enter into details of technique. Some generalizations, however, call for notice.

The predetermining of the patient's probable tolerance involves the consideration of many factors. At best we start with an intelligent guess and apply a large margin of safety. Pacini [5] gives these factors as:

1. Endocrine type of patient (light or dark).
2. Sex.
3. Age.
4. Part rayed.

He says: "Speaking generally, light people respond more promptly than dark; females than males; the young sooner than the old; and the regions usually protected from the light and of high nervous sensibility, quicker than other parts."

Pacini gives the following as the order of sensitiveness of different parts, the figure after the name of each part being reciprocal of the sensitiveness as judged by the time required to produce a given degree of reaction.

Chest (1), abdomen (1), back (1 +), groin (1 +), anterior arm (1½), posterior arm (1¾), posterior leg (1¾), anterior leg (2), dorsum of hands (5), palms of hands (15), sole of foot (25).

When general irradiation is intended it is the sound practice to commence by fractional exposures; at each sitting exposing a fresh part and increasing the exposure of previously treated regions, until the whole body may be irradiated. This has been the practice of Rollier in heliotherapy, and it finds its experimental justification in the work of Levy (1916) and of Gassul (1920) who have shown that general irradiation of the whole body at the first sitting may lead to dangerous visceral engorgements.

The following classification of the primary skin reactions is quoted from "Handbook on Quartz Light Therapy." [6] It is so clear as to require no comment.

A first degree erythema is a reaction so slight that it causes no subjective symptoms. The reddening of the skin is very slight and is not followed by visible exfoliation.

A second degree erythema is a reaction accompanied by symptoms of mild sunburn. The reddening is plainly visible and after the reaction subsides it is followed by a granular exfoliation.

A third degree erythema is a reaction intense enough to cause symp-

[5] Loc. cit.
[6] Published by Hanovia Chemical and Manufacturing Company.

toms of severe sunburn. The reddening is intense and the epidermis can be peeled off in large strips.

A fourth degree erythema is a blister production.

When a first degree erythema is produced the reaction is so slight that similar treatments can be given daily. A second degree erythema can also be applied daily. It might be well, however, to allow two days to elapse. A third degree erythema necessarily will take 3 to 4 days to clear up. Judgment should be used in cases of this kind. A fourth degree erythema generally takes from 1 week to 10 days to clear up, depending entirely upon the tolerance of the patient's skin.

In only a very sensitive patient will the reddening (erythema) show during treatment; it generally appears 3 or 4 hours afterwards. A first degree erythema is not generally produced in general body radiations. The object in view when administering general radiations for systemic effect is to produce a gradual deep tanning of the entire body without vesication or undue peeling. It is sometimes recommended after 12 to 15 exposures that an intermission be made of 3 to 4 weeks before resuming treatments. When beginning treatments again short exposures must be given at first, since the patient has by that time lost most of the tan, and with it the immunity to burning.

The eyes should be carefully protected. Goggles may be worn by the patient or small wads of cotton placed over the eyes. The most simple method in cases of adults is to keep the eyes shut when facing towards the light.

When bactericidal action—necessarily superficial—is desired, the water-cooled lamp is the instrument of necessity. The same is practically true whenever intensive action of the lethal rays, of short wave length, is indicated. So that for intense, focal, caustic irradiation, producing destructive erythema, we must use the water-cooled lamp.

In some cases special filters are employed to insure that the lethal rays are completely excluded in systemic irradiation. As our knowledge of the action of different regions of the ultraviolet becomes more specific, it is possible that the practice of selective filtering will come into general usage. It is easy to obtain filters which will isolate individual emission lines of the mercury arc spectrum. Work is being done along these lines in many places and especially in France. But, so far, nothing of immediate applicability has been published. (See Chapter 4.)

Outline of Therapeutic Technique.

When starting treatment with ultraviolet rays, there is a feeling of warmth, later a slight tingling is experienced and by strong radiation blistering of the skin results. This effect usually disappears in two or three days. There is no visible change during the treatment of dry lesions, but moist surfaces such as bleeding or secreting wounds begin to dry up after a few minutes exposure. Usually in 2 to 4 hours after a treatment, redness appears on the part which has been exposed.

The erythema persists for 2 or 3 days and is followed by a tan. Moist surfaces which have been dried by the effect of the light remain dry. During the first "general" treatment, that is, exposure of large areas, there is no visible change, or merely a slight reddening. In 3 or 4 hours if the radiation has been very strong, the exposed surface shows a decided redness, and blisters may develop. The redness decreases gradually and within 2 or 3 days, some pigmentation appears. Owing to the darkening of the skin thus produced, subsequent treatments are not usually accompanied by further reddening or blistering of the skin but there is increased tanning. If, however, the intervals between treatments are unduly long, or the treatment is very severe, the effect may be the same as resulting from the first treatment.

To ascertain the effect upon the skin, eyes, and general condition, Bach resorted to a heroic test. He applied the ultraviolet light with great intensity upon his own person, without protecting his eyes. An exposure of 30 minutes was given at a distance of 16-20 inches from a 3000 candle-power lamp. The head and body were treated alternately. After 3 minutes there was a sensation of warmth and after 10 minutes a burning sensation at the place of exposure. An intense reddening appeared in 2 or 3 hours after the treatment. This discoloration disappeared in 3 days. There was no blistering, but the epidermis became hard and dry, and peeled off within a week, being replaced by a new epidermis which was elastic and brown. The conjunctiva commenced to redden in about 2 hours after the treatment, becoming inflamed and painful, but the inflammation disappeared in about 3 days without treatment. Immediately after the treatment and for days thereafter there was a feeling of freshness and of increased energy. This effect perhaps may be expressed as a case of over-stimulation of a person in good health.

In actual practice the ultraviolet radiation is used either as the principal remedial agent, or as an adjuvant to other therapeutic measures. It is used either locally, for the treatment of external or accessible morbid conditions, usually with the water-cooled lamp, or generally (systemic radiation), with the air-cooled lamp. It is often found advantageous to associate the local, caustic effect of the lethal ray with general stimulation by systemic radiation. We shall not attempt to give a list even of those morbid conditions which are generally accepted as more or less amenable to treatment by this method. We shall content ourselves with a brief account of its application in some illustrative conditions.

It is natural to begin with the disease in the attack on which radiation won its spurs,—tuberculosis.

The great stream of evidence in promise of the method rises in two sources. These are, first, the pioneer work of Finsen on the treatment of local tubercular conditions, especially lupus vulgaris, with intensive arc radiation; and second, the labors of Rollier, in the Alps, on heliotherapy for "surgical" tuberculosis (especially joint and bone disease), and for tuberculosis of the viscera, especially pulmonary phthisis.

The Finsen technique led directly to the modern treatment by the quartz lamp, and especially by the water-cooled lamp, which has superseded the arc.

Rollier and his followers still use heliotherapy. But sunlight of alpine quality is not generally available. It is fortunate, therefore, that dwellers in towns and lowlands find, in the radiation of the air-cooled quartz lamp, a substitute which is, in the opinion of most, at least the equal of sunlight, and which is thought, by some, to have definite superiority over its natural rival.

In some classes of cases radiant heat is combined with ultraviolet radiation. This is a close imitation of sunlight, and is especially valuable in surgical tuberculosis.

In no condition is caution in initiating the treatment more necessary than in visceral tuberculosis. The patient's reaction must be very carefully studied. Fractional habituation is imperative.

The hectic fever generally subsides in less than a month and, if the treatment is continued, this first return to a normal temperature curve is permanent in 50 per cent of the cases. In seventy-seven cases, "many with gross pulmonary lesions," reported by Stewart,[7] two-thirds showed improvement. In the same paper it is stated that of forty-seven cases of intestinal tuberculosis in soldiers, all but five recovered or were permanently improved.

In all tuberculous conditions systemic radiation is used. In tuberculosis of the skin, in joint diseases with sinuses, in tuberculous ulcers and fistulæ, intensive local radiation is also employed, either with the air-cooled lamp, or with the water-cooled lamp, using, in the latter case suitable quartz applications.

It is a natural transition from treatment of tuberculosis of the skin to that of other dermatoses. In the treatment of skin diseases the ultraviolet ray has proved a veritable godsend. Many persons maintain a cheerful front when suffering from serious internal, and therefore, invisible lesions, but it is difficult to be or to appear as happy when exposing to the public view the disfiguring and often repulsive lesions of skin disease.

Here again both air and water-cooled lamps are employed, either air-cooled alone as, e.g., in lupus erythematosus or both, as in furunculosis. In some types of cases the treatment by ultraviolet is combined with other radiations, as with radiant heat, e.g., in acne vulgaris, or with X-rays.[8]

As we have repeatedly mentioned, the field for this method is daily expanding, and it would be futile to attempt, here, to survey it even in outline. It is true that there are diseases, even chronic diseases, in which ultraviolet rays are of no benefit. But there are few, if any, chronic diseases in which they can, when prudently applied, be harmful.

[7] Canadian Med. Ass. J., Jan. 1923.

[8] For a full discussion of the use of ultraviolet therapy in the treatment of skin disease, the reader is referred to Bernstein, Ultraviolet Rays in Modern Dermatology; Achey and Gorrecht, Lancaster, Pa., 1918. Saleeby, Sunlight and Health, New York, 1924, is of collateral interest.

Sampson [9] seems to feel that diabetes mellitus is an exception, though he admits that this has not been the experience of all others. In fact ultraviolet radiation has been successfully used in the treatment of diabetic gangrene.[10] McCaskey, however, agrees with Sampson.[11] The experience of the latter has been that diabetics exposed to ultraviolet radiation, suffer from a severe general reaction. This is so characteristic that, when such a reaction occurs, Sampson suspects the existence of diabetes, and this suspicion has almost always been confirmed by the discovery of hyperglycemia, even in the absence of glycosuria. The reaction is described as resembling anaphylactic shock.[12] Sampson says: "The untoward reaction of diabetic to the actinic ray may be anything from chilly sensations and a mild headache to a condition simulating surgical shock or even anaphylaxis. There is generally a marked malaise for 2 or 3 days and Plank states that he has observed amnesia and loss of will power."

Any of our readers who are familiar with insulin treatment will notice a resemblance between these symptoms and those of induced hypoglycemia. The matter certainly calls for careful investigation.

Ultraviolet in Deficiency Diseases, Rickets, etc.

We must now pass to the growing point of ultraviolet therapy or, to change the metaphor, we must go into the firing line. This is the use of ultraviolet light in the control of calcium and phosphorus metabolism and, through this control, in the treatment of conditions where this metabolism is defective. The most important of these conditions are rickets, tetany, and deficient new bone formation in fracture healing.

Closely associated with this question is that of the vitamin deficiency diseases, i.e., diseases which are believed to be due to the insufficiency in the diet of those elusive accessory factors discovered by Hopkins, and prematurely named "vitamines" by Funk. The name is unfortunate but it has "stuck," and we must abide by popular usage.

Let us refresh our memories on this important subject, especially with reference to the fat-soluble factor.

Vitamin A (fat soluble) is found in green plants, in milk, in certain vegetable oils such as oil of millet, in cod liver oil and in many other substances, nearly always associated with yellow pigment. Deficiency of this in the diet causes a special eye disease known as xerophthalmia. It was for long thought that the vitamin that is necessary to prevent xerophthalmia was identical with that which is necessary for growth and reproduction. Doubt has now been thrown on this as we shall presently see. The two are, however, present together in natural foods.

When young rats were fed on a diet deficient in this natural combination of vitamins, they failed in growth, and developed xerophthalmia. Furthermore they suffered from a bone condition apparently identical

[9] Physiotherapy Technic, St. Louis, 1923.
[10] Bach, loc. cit.
[11] N. Y. Med. J., Dec. 17, 1919.
[12] McCaskey, loc. cit.

with rickets.[13] This condition was prevented or cured by giving cod liver oil.

In 1918 Hess, McCann and Pappenheimer [14] reported that they were unable to produce rickets by using a diet, deficient in vitamin A, but otherwise adequate.

Here threatened a deadlock. The explanation seems to have been that the rats used by Hess and his collaborators were exposed to bright light. When the experimental animals receive only room light rickets invariably occur.

But that the deprivation of light is not in nature the usual cause of rickets is shown by the fact that an adequate diet will protect rats from rickets, even if they are kept in the dark.

However, observations soon began to accumulate, showing that inadequate sunlight was a potent cause of rickets in human children. There is no doubt that it is frequently associated with a diet deficient in the appropriate vitamin.

In 1920 Hess and Unger [15] reported that rickets develops in children, notwithstanding an abundance of fresh air. Liberal allowance of light in glass cubicles failed to prevent it. These workers also failed to benefit rickets by ultraviolet radiation. They, therefore, expressed the opinion that ultraviolet radiation could not replace sunlight, an opinion they recanted soon afterwards, for in 1921, in a preliminary note on the cure of rickets by sunlight,[16] they use the expression ". . . encouraged by our results in curing rickets by means of the ultraviolet ray. . . ." Huldschinsky had, in 1919, proved that infantile rickets could be cured by the ultraviolet radiation from the quartz lamp.[17] Hess and Unger attribute the seasonal variation in the occurrence of rickets to the variation in the intensity of sunlight.[18]

Studying the prevention of rickets in the rat by means of radiation with the mercury vapor quartz lamp, Powers, Park, Shipley, McCollum and Simmonds [19] found that the effects of the radiations of the mercury vapor quartz lamp (Hanovia, Alpine type) on the growth and calcification of the skeleton of the rat, and on the animal as a whole, seem to be familiar if not identical with those brought about by direct sunlight and by cod-liver oil.

The effect of radiation with the quartz mercury vapor lamp on the growth of rats fed on a diet deficient in vitamin A was investigated by Margaret Hume.[20]

Irradiation with the quartz lamp prolonged the growth of rats on

[13] McCollum and Davis, J. Biol. Chem. 1914, *19*, 245, and Vital Factors of Foods, by Ellis and Macleod, N. Y., 1922.
[14] J. Biol. Chem. 1921, *148*, 2.
[15] J. Am. Med. Assoc. 1920, *74*, 217-223.
[16] J. Am. Med. Assoc. 1921, *77*, 39.
[17] Deutsch. Med. Woch. 1919, *45*, 712.
[18] Am. J. Dis. Children; 1921, *22*, 186. Cf. a similar opinion for infantile spasmophilia expressed by Worringer, Compt. rend. soc. biol. 1923, *88*, 1160-3. See also Hess, J. Am. Med. Assoc. 1925, *84*, 1014.
[19] Proc. Soc. Exptl. Biol. Med. 1921, *19*, 120.
[20] Lancet 1922, II, 1318; Chem. Abs. 1923, *17*, 803.

a diet free, or almost free from vitamin A. Without irradiation growth ceased to be normal after 7-10 days, with irradiation it continued normal for 35-50 days. Symptoms of vitamin A deficiency then set in. Attempts to relieve symptoms of vitamin deficiency by irradiation of animals which had long (over 90 days) been on a deficient diet failed. It is concluded that there is an interaction of light and vitamin A in the growth of rats, but no photosynthesis of vitamin. The vitamin is economized or the vitamin stores are forced to yield it up at a rate sufficient to produce normal growth until they are wholly exhausted. This was confirmed by Goldblatt and Soames,[21] for 4 to 5 weeks after being placed on a diet deficient in the fat-soluble vitamin rats radiated with the quartz lamp grow at the normal rate. Slight but temporary improvement is noted on radiating rats which have ceased to grow as a result of fat-soluble vitamin deficiency. Radiation is thus no substitute for the viamin but in some way economizes it in its action.

A study of light waves in relation to their protective action in rickets was made by Pappenheimer and Weinstock.[22] White rats fed a rickets-producing diet were protected against rickets by daily irradiation for 2 minutes by the mercury vapor quartz lamp at a distance of 3 feet and a voltage of 76. By interposing standard glass filters it was determined that rays as long as 334 μμ have little or no protective action; the effective rays begin in the neighborhood of 313 μμ.

The use of the carbon arc light in the prevention of rickets was reported on by Hess and Unger.[23] The treatment resulted in a rapid subsidence of the signs of rickets accompanied by a constant increase in the inorganic phosphates of the blood. Attempts to cure rickets by adding dipotassium hydrogen phosphate to ordinary diet was unsuccessful, but it is thought that previous administration of phosphate hastened the cure by the arc light. Schultzer and Sonne have reported on the prophylactic action of light in experimental rickets.[24]

Similar results were obtained by Eckstein.[25] The radiation from the carbon arc lamp prevents and cures rickets in rats, thus confirming the work of previous workers.[26] Rats on rachitic diets show atrophy of the skin, muscle, thymus and liver. There is also a loss of fat about the adrenals. In general, there are all the signs of inanition.

The effect of ultraviolet rays on rats, deprived of vitamin A in their diet was the subject of investigation by Sheets and Fund.[27] Rats, fed a diet deficient in vitamin A, were given a 3-5 minute daily exposure to ultraviolet. The rays prevented rickets, permitted a normal rate of growth, but did not prevent the development of xerophthalmia.

Powers, Park and Simmonds [28] examined the influence of light and darkness upon the development of xerophthalmia in the rat. Rats were

[21] Lancet 1922, II, 1321; Chem. Abs. 1923, *17*, 803.
[22] Proc. Soc. Exptl. Biol. Med. 1922, *20*, 14; Chem. Abs. 1923, *17*, 3364.
[23] J. Am. Med. Assoc. 1922, *78*, 1596; Chem. Abs. 1923, *17*, 2327.
[24] Acta Med. Scand. 1924, Suppl. VII, 97.
[25] Arch. Kinderheilk. 1924, *74*, 1; Chem. Abs. 1924, *18*, 3207.
[26] Cf., the same worker as reported on page 302, this chapter.
[27] Proc. Soc. Exptl. Biol. Med. 1922, *20*, 80; Chem. Abs. 1923, *17*, 3528.
[28] Proc. Soc. Exptl. Biol. Med. 1922, *20*, 81; Chem. Abs. 1923, *17*, 3528.

fed a diet deficient in phosphorus and in vitamin A; all groups exposed to roomlight, darkness, or the violet lamp developed xerophthalmia and became emaciated. Sunlight prevented rickets, promoted bodily vapor, and delayed the development of xerophthalmia. Cod-liver oil contains an antixerophthalmic as well as an antirachitic factor.

A study of rats, on a normal diet, irradiated daily by the mercury-vapor quartz lamp, or kept in darkness, was made by Goldblatt and Soames.[29] Two litters of rats were placed on normal diets containing an optimal amount of calcium phosphorus and the "fat-soluble organic factor." In the diet of one litter this last was supplied by cod-liver oil, while for the other, two diets, one containing butter and the other cod-liver oil, were used. One half of each litter was kept in the dark and the other in daylight with the addition of a daily irradiation for 20 minutes under a quartz lamp. No appreciable difference was found between the growth of the two groups or the histology and calcium content of the bones.

According to Goldblatt and Soames [30] rats on a diet deficient in fat-soluble organic factor grow normally, and their bones develop and calcify normally provided they are irradiated for about 10 minutes daily by a quartz lamp. When the fat-soluble organic factor is completely absent, the rats show improvement after treatment with light rays, but normality is not reached.

Eckstein [31] introduces a discordant note. He reports that experiments with controls show that the growth of young white rats, as measured by length and weight as well as development, are independent of the quality of natural light (red, blue-violet or gray) and of its intensity. These results are in accord with those of J. Loeb. Artificial ultraviolet light produced a retardation in the growth of these animals. Animals on a vitamin-free diet died sooner after ultraviolet radiation than those unexposed to the rays. Animals kept in the dark showed no rickets on external examination.[32]

Allenbach and Simon [33] report that three groups (six each) of young albino rats were fed: (1) normal diet, (2) McCollum's diet No. 3143 [34] rich in calcium and low in phosphorus and in fat-soluble vitamins, and (3) same as (2) but exposed daily to ultraviolet rays. After 49 days group (1) was much bigger and heavier than (2) and (3), the latter

[29] Biochem. J. 1923, *17*, 294; Chem. Abs. 1923, *17*, 3696. Steenbock, Hart and Jones have considered the effect of sunlight on the growth of pigs given restricted rations, J. Biol. Chem. 1924, *61*, 775, and Luce, Biochem. J. 1924, *18*, 1279, has reported on the influence of sunlight on cows with respect to the antirachitic value of milk.

[30] Biochem. J. 1923, *17*, 622; Chem. Abs. 1924, 409.

[31] Chem. Abs. 1923, *17*, 3526; Arch. Kinderheilk. 1923, *73*, 1.

[32] Cf. McCollum, Park, et al., Chem. Abs. 1921, *15*, 3611.

[33] Rev. Hyg. Soc. Strasbourg 1923, *81*, 670; Bull. Soc. Hyg. Aliment. 1923, *11*, 124; Chem. Abs. 1923, *17*, 2306. That irradiation has some effect on calcium and phosphorus metabolism is demonstrated by Henderson, Biochem. J. 1925, *19*, 52. On a poorly balanced diet (P_2O_5: Ca: Mg = 3: 1: 1), a pig submitted to 1 hour's irradiation daily for 24 days with a carbon arc lamp definitely increased the calcium-phosphorus retention. No corresponding increase in body weight occurred.

[34] Chem. Abs. 1921, *15*, 3667.

two being practically the same. Radio-photographs showed in (2) and (3) enlargement of the cartilage but no well defined deformation of the bones.

According to Steenbock and Nelson [35] antirachitic agents (aërated cod-liver oil, ultraviolet rays) will restore growth in rats which have been maintained on a diet devoid of the fat-soluble vitamin, but will not postpone failure due to ophthalmia. These results support the view that cod-liver oil contains two vitamins, viz., vitamin A and the antirachitic factor. The following results were obtained by Nelson and Steenbock [36] with rats kept on a diet lacking the antirachitic factor. Non-irradiated animals showed normal growth when placed in the same cage with irradiated animals, or when placed in a jar of which the false bottom (galvanized iron wire screen) had been irradiated, but not when kept in a jar of which the air only had been irradiated. The screen effect was not obtained with new screens and is, therefore, probably due to a slight (although invisible) contamination of the latter by the animals previously kept on them. It is necessary for the animals to be actually in contact with the irradiated screen, and the possibility is therefore suggested that the effect is brought about by the ingestion by the animals of traces of excreta, adherent to the screens and rendered active by irradiation.

The nutritional requirements of baby chicks, and the relation of light to the growth of the chicken, were studied by Hart, Steenbock, Lepkovsky and Halpin.[37] The basal ration containing in 100 parts;—97 of white corn, two of calcium carbonate and one of common salt—and separator skim milk was given *ad libitum*. This ration has invariably led to cessation of growth and symptoms of rickets or leg weakness. Five groups of chicks were studied: group I was kept in a dimly lighted basement; group II had all day access to sunlight; groups III and IV received 10 and 60 minutes respectively exposure to the sunlight; and group V was radiated daily for 10 minutes, by the rays of a quartz lamp. Those receiving no sunlight died in 6 weeks, reaching weights of approximately 100 grams. In group II, five of the chicks reached weights of approximately 250 grams in 8 weeks. Group III was more like group I in general behavior, while the chicks in groups IV and V grew better and lasted longer than those in groups I and III, but were not equal as a group of the all day sunlight group II. It is thus apparent "that light can play an important part in the rearing of baby chicks, acting as a supplement or the equivalent to the antirachitic factor of foodstuffs." From limited data it appears that thirty minutes daily exposure to direct sunlight was much more potent in furnishing the antirachitic equivalent than was fresh green clover equivalent in dry matter to 5 per cent of a synthetic ration (containing 18 per cent of alcohol extracted casein, 60 per cent of dextrin,

[35] J. Biol. Chem. 1923, *56*, 355; Chem. Abs. 1924, *18*, 1320 and 2191.

[36] J. Biol. Chem. 1925, *62*, 575. Note Steenbock, Nelson and Black, J. Biol. Chem. 1924, *62*, 275, for modification of technique in the determination of vitamin A, involving irradiation of animals with ultraviolet.

[37] J. Biol. Chem. 1923, *58*, 33; Chem. Abs. 1924, *18*, 549; 1922, *16*, 2713. See also Chapter 15.

5 per cent of salt mixture, 2 per cent of agar and 15 per cent of dried brewer's yeast.

Hoag [38] treated infantile tetany with ultraviolet radiation. The return of the serum calcium to about 10 milligrams per cent was used to judge the completeness of the cure. Cod-liver oil increased the calcium over a period of several weeks while ultraviolet rays caused a progressive and permanent relief paralleled by the return of the serum calcium to normal within 2 weeks.

It has long been known that rickets and tetany are closely related to defects in calcium and phosphorus metabolism.

Kramer and Boone [39] showed that the cure of rickets in children by exposure to sunlight was accompanied by a return of the calcium and phosphorus of the serum to normal values.

According to Orr, Holt, Wilkins and Boone,[40] metabolism studies show that infants with active rickets fail to retain calcium and phosphorus although an adequate amount is present in the diet. Ultraviolet radiation causes large amounts of these elements to be retained in the body. Increased amounts of calcium and phosphorus are found in the urine after ultraviolet radiation, indicating an increased absorption from the intestine. It is argued that defective absorption from intestine found in active rickets is the cause of the low calcium and phosphorus found in the serum, and is the ultimate cause of the defective calcification of the bones. Vignard, Mouriquand, Chassard and Bernheim [41] publish two examples taken from clinical practice in which ultraviolet ray treatment of rickets promoted precipitation of calcium at the junction of bone and cartilage, as clearly brought out by radiography.

Lesné, deGennes and Guillaumin [42] report that the mean calcium content of normal infants from 2 months to 2 years of age, oscillates between 100 and 120 milligrams per liter of serum. In twenty infants with rickets the calcium content ranges from 79 to 104 milligrams with an average of about 92. Two children of 3 and 8 years with irreducible rachitic deformations had the normal amount of calcium or slightly higher (118 and 114 milligrams respectively). The calcium content of the serum is not modified by the ingestion of calcium chloride, or by changes in temperature. Ten infants were subjected daily to the radiations of a 1200 c.p. arc lamp at a distance of 1.2 m.

[38] Am. J. Diseases Children 1923, *26,* 186; Chem. Abs. 1923, *17,* 3539.
[39] Proc. Soc. Exptl. Med. 1922, *20,* 87.
[40] Am. J. Diseases Children 1923, *26,* 362; Chem. Abs. 1924, *18,* 105.
[41] Lyon Médical 1923, *132,* 1021; Chem. Abs. 1924, *18,* 2382.
[42] Compt. rend 1923, *177,* 291; Chem. Abs. 1923, *17,* 3540; see also Howland and Kramer, Chem. Abs. 1923, *17,* 413; Hess and Unger, Chem. Abs. 1920, *14,* 3709. The administration of eosin is claimed by György and Gottlieb, Klin. Wochschr. 1923, *2,* 1302, to sensitize the patient so that ultraviolet is more effective. Infants afflicted with rickets recovered more rapidly when irradiated, if first treated with eosin. Studies made by Hinrichs, J. Exptl. Zoöl. 1924, *41,* 21, on protozoa, coelenterates, platyhelminths and annelids show that ultraviolet has a differential action on living organisms. Photodynamic sensitization with eosin renders such organisms differentially susceptible to light in the visible region of the spectrum. Photolytic disintegration can be used as a means of demonstrating the presence of an axial gradient in organisms.

for 30 minutes. The ultraviolet rays alone were efficacious. After eight such radiations the calcium content of the serum in seven cases was decidedly increased and after 24 radiations was well up to normal in eight of the cases. The two remaining infants showed no increase in the calcium content and these subjects were both dark skinned. Deficiency of calcium in the serum is evidence, but not the cause of rickets. Deficiency of phosphorus and inability to fix calcium are probably the conditions which lead to rickets and these conditions are relieved by ultraviolet radiation.

In this connection interesting results on the effect of ultraviolet rays on the *condition* of calcium in the blood are reported by Clark.[43] The diffusible calcium of blood serum, measured by dialysis in collodion sacs against physiologic sodium chloride, was found to be higher after the serum was exposed to radiation of quartz mercury arc. The diffusible calcium in rabbit serum rose from 38 to 58 per cent; in dog serum from 44 to 53 per cent.

Kramer, Casparis and Howland[44] found that before treatment of rickets with a quartz lamp the inorganic phosphorus of the serum was from 2.7 to 3.2 milligrams. Under treatment it gradually increased to a maximum of 6 milligrams.

Studies by Hart, Steenbock and Elvehjem[45] on the effect of light upon phosphorus and calcium equilibrium in lactating animals have a direct bearing on this aspect of our subject matter. They find that ultraviolet rays influences the storage of calcium and phosphorus in lactating animals. Exposure to ultraviolet of animals which, owing to dietetic deficiency were excreting more calcium than they were assimilating, resulted in the reversal of this condition (technically expressed: a negative calcium balance was made positive). The inorganic phosphorus of the blood was simultaneously increased.[46]

Analogous observations have been made in hay-fever hyperesthetic rhinitis and the asthmas, by Novak and Hollender.[47] The ionic calcium content of the blood serum is invariably low in hyperesthetic rhinitis. There are also certain cases of hayfever and asthma which show a low calcium content. Calcium alone does not influence these conditions. Calcium lactate combined with thyroid extract affords temporary relief in all cases of hyperesthetic rhinitis and in some cases of hay-fever and bronchial asthma. Exposure to the mercury arc, together with the combined calcium thyroid therapy, appears to fix permanently the ionic calcium content of the blood serum.

After fracture of a bone, and during the period of repair there occurs in adults an increase in the inorganic phosphorus of the blood as well as of the calcium. When this fails, delayed union of the fragments results. Tisdall and Harris have shown, by experiments on dogs

[43] Am. J. Hyg. 1923, *3*, 481; Chem. Abs. 1924, *18*, 2366.
[44] Am. J. Diseases Children 1922, *24*, 20; Chem. Abs. 1923, *17*, 817.
[45] J. Biol. Chem. 1924, *62*, 117.
[46] Note that recurrence of "inorganic" and "diffusible" as applied to calcium and phosphorus contents of the blood, when improvement sets in during rickets and the like. It seems to be the keynote.
[47] J. Am. Med. Assoc. 1923, *81*, 2003; Chem. Abs. 1924, 1153.

and by observations on human patients, that the mobilization and utilization of calcium and phosphorus in these cases is promoted by radiation with ultraviolet.

An interesting observation on the effect of ultraviolet rays on normal rabbits was made by Grant and Gates.[48] Rabbits were daily exposed for 30 minutes to the unfiltered rays of a quartz mercury arc lamp over a period of 3 to 7 weeks. The parathyroid glands of rayed animals were 32 per cent heavier than those of the controls. Blood calcium increased from 11.9 milligrams per 100 centimeters to 12.0 milligrams per 100 centimeters in 22 days.

Alpern [49] reports that the water and sugar in the blood of normal animals increase as the result of ultraviolet radiation. Less marked results are obtained in the fat content. There is generally an increase in the light petroleum and ethyl alcohol fractions without corresponding increase in the cholesterol content. The blood of animals deprived of vitamins exhibits the same changes.

Irradiated Substances.

The most sensational among these sufficiently remarkable developments is the discovery that irradiation of a ration will sometimes make up for a deficiency in it of vitamin A.

Hume and Smith were very near this discovery when they reported [50] that rats (fed on a diet deficient in fat-soluble vitamin) kept in glass jars which had been exposed to quartz lamps for 10 minutes every second day, showed a prolongation of normal growth over controls not so treated. Rats exposed to the air containing ozone drawn over the quartz lamps and passed through three milligrams of glass tubing, 0.8 centimeters bore, showed poorer growth than the control animals.[51] But they had overlooked the real cause of the result that they had observed. Webster and Hill,[52] contrary to the results of Hume and Smith, found that the growth of rats on a diet, deficient in vitamin A only, could not be stimulated by radiation (from a quartz lamp) of the air in the jar in which the animal lived. Exposure for 30 minutes daily to air led from the enclosure of the mercury-vapor lamp failed to influence rickets in young rats fed on a deficient diet, while exposure to the light of the lamp had the well known curative effect.

[48] Proc. Soc. Exptl. Biol. 1924, *21*, 230.

[49] Strahlentherapie 1923, *15*, 661. A highly interesting observation has been made by Findlay and Maclean, Biochem. J. 1925, *19*, 63, on the bactericidal action of the blood in certain dietary deficiencies. The blood of normal rats, tested against *Staphylococcus aureus*, shows a killing power of about 70 per cent. Rats fed on a diet deficient in vitamin A and the antirachitic factor show a reduction in the bactericidal power of the blood only after the onset of xerophthalmia. If exposed to ultraviolet rays, the onset of bacterial infection in such rats and the reduction in the bacterial power of the blood are delayed. On a minus vitamin B diet, rats show a reduction in the bactericidal power of the blood unassociated with bacterial infection.

[50] Biochem. J. 1923, *17*, 364; Chem. Abs. 1923, *17*, 3696.

[51] Cf. Chem. Abs. 1923, *17*, 803.

[52] Proc. Physiol. Soc., Journal of Physiol. 1923, *57*, lxxviii; Chem. Abs. 1924, *18*, 278.

Hume and Smith returned to the charge and reported [53] that rats kept on a diet deficient in fat-soluble vitamins and housed in previously irradiated glass jars containing sawdust showed growth as good as that shown by directly irradiated animals. In the absence of sawdust, this growth does not take place. When the sawdust is replaced by a piece of deal board, partial growth takes place. The degree of calcification is directly proportional to the amount of growth.

But they had missed their chance, for in the meantime Steenbock and Black had discovered and applied for a patent on a process for the induction of growth-promoting and calcifying properties in a ration, by exposure to radiation from a quartz lamp.[54]

Proceeding on the assumption that failure of growth on basal synthetic rations without the effect of illumination was due to a condition fundamentally the same as rickets, experiments were initiated in which such rations were illuminated and then fed to rats. The result was that illumination of the ration caused it to become growth promoting and, in addition, it was found that the ash content of the bones of rats receiving such a ration was increased in percentage over that of rats receiving the non-radiated ration. It was also found that irradiation of fats, otherwise inactive in preventing rickets, caused them to become active, and that rations which ordinarily produced wide rachitic metaphysis in the shaft bones of rats became antirachitic and promptly effected a rapid and complete healing of the lesion. These facts have now been correlated with what is known of the properties of antirachitic vitamin and found in substantial agreement.[55]

Steenbock and Daniels,[56] discussing the therapeutic possibilities of this food-irradiation method, conclude: that the sterols in food carry the activation which explains the wide range of materials which can be activated (wheat, rolled oats, corn, hominy, starch foods, meat, milk and egg yolk and especially the vegetable oils).[57]

A fascinating suggestion as to the fundamental property common to all these curative and preventive agents is contained in an article by Kugelmass and McQuarrie,[58] which is thus summarized: [59]

This study is an attempt to learn the common property between radiant energy of the sun and the quartz lamp and antirachitic remedies such as cod-liver oil, egg yolk, etc. The data presented show that the substances curative of rickets, upon oxidation, blacken sensitive plates through quartz but not through glass screens. This phenomenon is

[53] Biochem. J. 1924, *18*, 1334.

[54] J. Biol. Chem. 1924, *61*, 405; Chem. Abs. *18*, 1328 and 3640; Science 1924, *60*, 224. Confirmed by Steenbock and Nelson, J. Biol. Chem. 1924, *62*, 209.

[55] To protect the interests of the public in the possible commercial use of these findings, applications for Letters Patent, both as to processes and products, have been filed with the U. S. Patent Office and will be handled through the Univ. of Wisconsin.

[56] J. Am. Med. Assoc. 1925, 84, *15*, 1093.

[57] On the same subject see Drummond, Rosenheim and Coward, J. S. C. I. 1925, *44*, 135 T.

[58] Science 1924, *60*, *272*.

[59] Chem. Abs. 1925, *19*, 353.

undoubtedly due to the emission of ultraviolet radiation.[59a] The interposition of quartz plates excludes the effect of reducing vapors which otherwise blacken the sensitive plate. The non-blackening through glass screens excludes the emission of both radioactive and visible rays. The conclusion is that upon oxidation ultraviolet rays are produced. The degree of blackening is apparently a function of the rate of oxidation, for the intensity of the image from vigorous oxidation is greater than that from spontaneous oxidation within a given time. The blackening is also a function of H-ion concentration, for the intensity of the image is greater from alkaline medium than from neutral or acid mediums. The experimental data further show that the oxidized substances curative of rickets when exposed to ultraviolet radiation liberate oxygen. Therefore the photochemical reaction appears to be reversible and may be expressed thus: O + rickets-curing substances $\rightleftarrows$ oxy-substances + ultraviolet rays. These experiments point strongly to the common property of emitting ultraviolet rays, of cod-liver oil, egg yolk, sperm oil, bile, on the one hand and of sunlight or quartz lamp radiations on the other, as a basis for their identical curative action in rickets.

This must be read in connection with the results reported by Drummond and Coward.[60] No action on photographic plates from cod-liver oil through silica has been detected. Definite action was observed when the plate had been exposed directly to the vapor of certain oils and many other substances. Silica vessels that have been exposed to ultraviolet light for a very short time emit radiations which also affect plates, and this action has been detected even as long as 20 days after the irradiation. Irradiating cod-liver oil either directly or through silica does not give it any power to fog a photographic plate through silica. The effect obtained by other workers and supposed to be due to the cod-liver oil may thus have been due to a previous exposure of their silica vessels to light. Direct irradiation of rats which had become steady in weight on a diet deficient in Vitamin A has made them resume growth, but no effect has been produced on similar rats by letting them breathe irradiated air. Freshly irradiated sawdust daily has no effect if the rats are not allowed to eat it, and if they are allowed to do so, it only gives them a very temporary stimulus. Irradiation of vitamin-free diet has caused resumption of growth in rats; irradiation of the starch and casein respectively has been without effect, irradiation of hardened fat (a bean oil) has produced slight growth-promoting action. In collaboration with Rosenheim,[61] cholesterol was radiated and found to induce resumption of growth in a dosage of 1 milligram per day in several rats, while a control test of 1 milligram per day of non-irradiated cholesterol had no effect on seven other rats. Hess Weinstock, and Helman [62] found that phytosterol prepared from the unsaponifiable fraction of cottonseed oil, which itself had no antirachitic prop-

[59a] While this volume was in press Kugelmass and McQuarrie, Science, 1925, *62*, 87 altered their views, now ascribing the action on the plate to "Russell Effect." Note also West and Bishop, ibid., 86.

[60] J. S. C. I. 1925, *255*.

[61] J. S. C. I. 1925, *44*, 123 T.

[62] J. Biol. Chem., 1925, *63*, 305.

erties, acquired such properties when irradiated, in aqueous suspension, with ultraviolet; similar results were obtained with cholesterol isolated from brain tissue and with lanolin. Hess and M. Weinstock [62a] observed that antirachitic properties can be conferred, by ultraviolet irradiation, upon etiolated and green wheat and lettuce leaves, but not upon chlorophyll, hæmoglobin, red blood corpuscles, cream, glycerol, or the phosphatides of egg-yolk. They noted that the same results are obtained by the action of ultraviolet on cottonseed and linseed oils, wheat which had been grown in the dark, and various green vegetables.[62b] The activation of vegetable oils by irradiation can be carried out equally well in an atmosphere of nitrogen; in such activated oils the active substance is in the unsaponifiable fraction. Activation conferred by ultraviolet irradiation is retained for periods of weeks by the vegetables and for at least 6 months by the oils. In the absence of air, Spinka reports that butter irradiated by the ultraviolet of a mercury lamp does not lose its vitamin A activity. In presence of air, toxic substances are produced in the butter during irradiation, causing early death of the animals in whose diet it is incorporated. Vitamin B in neutral or weakly acid solutions is not destroyed by ultraviolet. Vitamin C in fresh lemon juice is not destroyed in absence of air, and even in presence of air only when the acidity of the solution is reduced is it destroyed. Vitamin D is remarkably resistant to ultraviolet irradiation.[62c]

At a meeting of New York Section of the American Chemical Society, January 9, 1925, Dr. Alfred F. Hess, Clinical Professor of Pediatrics at University and Bellevue Hospitals, New York, discussed the power of ultraviolet irradiation to impart antirachitic properties to inactive substances. He pointed out first that while for most diseases only one specific was known, for rickets there were two specifics of apparently widely different nature: cod-liver oil and ultraviolet rays. Only a very narrow range of wave-lengths in the neighborhood of 3050 Å is effective for the cure of rickets. After pointing out that rickets is characterised by non-calcification of the bones and low inorganic phosphorus Hess reviewed briefly the procedure used for experimenting with rickets in rats. This was as follows:

Rats about 28 days old and weighing 40 to 50 grams were used. They were fed a low phosphorus diet (75 milligrams) for a period of 4 weeks, some of them being fed with various substances which were to be tested for their protective action. These materials were given by pipette and not mixed with the diet. After 4 weeks the rats were X-rayed, then killed and examined. Hess commented on the fact that the action of ulraviolet rays on the organism is not local but that irradiation of one part affected the entire body; that is, the action is systemic. It has been found that if various foodstuffs are first irradiated by means of sunlight or a quartz mercury-vapor arc they have a

[62a] J. Biol. Chem., 1925, *63*, 297.

[62b] J. Biol. Chem. 1924, *62*, 301; Cf. Steenbock and Black, loc. cit. Hess, Am. J. Diseases Children, 1924, *28*, 517, reports that antirachitic potency is developed in cottonseed and linseed oils by raying with ultraviolet from a mercury vapor lamp, at a distance of 1 foot. The time period of exposure was one hour. Rayed mineral oil when fed in the same amounts gave negative results. Ozonated water and hydrogen peroxide showed no protection against rickets.

[62c] Biochem. Z. 1924, *153*, 197. Spinka's suggestion that the failure to grow of mice given irradiated butter as sole source of vitamin A was not necessarily due to destruction of this vitamin by the ultraviolet rays, Zilva contends (Biochem. Z. 1925, *155*, 333), is not in accordance with experimental data previously brought forward. See J. Chem. Soc. 1919, i, 461; 1921, i, 475; J. S. C. I. 1925, 259.

rickets-protective action which is similar to that obtained by direct irradiation of the animal. Cottonseed oil was exposed in thin layers for two minutes at a distance of one foot from the mercury-vapor lamp. This is not necessarily the minimum time for imparting antirachitic properties. Rats receiving the irradiated oil did not get rickets. Those receiving the same oil which had not been exposed to radiation developed rickets. Rickets is most prevalent in winter when the solar radiation has the least ultraviolet intensity. Especially in winter there is not much ultraviolet in the solar spectrum, under 3130 Å and there is none at all except at midday. Seventy-five per cent of New York babies are said to have rickets more or less at some time in their development. Irradiated oil was found still to be effective 6 months after its exposure to the light. Oxygen was found not to be necessary to activate the oil. Irradiated mineral oil, gelatin, air or water does not protect against rickets. Likewise irradiated blood serum, chlorophyll and hæmoglobin were ineffective. Irradiated wheat is antirachitic, but this is not due to the chlorophyll. Irradiated lettuce is also protective and it is of no consequence whether the lettuce is yellow or green. Cod-liver oil may be separated into saponifiable and unsaponifiable fractions. The antirachitic properties were found to be in the unsaponifiable fraction only. The same observation was made with linseed oil. The unsaponifiable material consists principally of cholesterol and phytosterol. Rats fed with irradiated cholesterol or phytosterol were found to be normal while those fed with the same substance which have not been exposed to the ultraviolet rays develop rickets. The skin of animals has much cholesterol, only the brain having more. This may account for the direct action of ultraviolet rays on the animal despite the fact that the ultraviolet radiation penetrates only a short distance. The activated cholesterol is taken up by the blood stream and distributed and fresh unactivated cholesterol brought to the skin. Hence the skin should perhaps be considered an organ instead of merely an inert covering.

Sherman suggested that the products obtained by irradiation of ordinary substances might have a wider significance than merely the prevention of rickets. It was suggested that possibly vitamins are ordinary substances activated in some manner. It seems that ultraviolet rays may not be the activating agency in all cases. It was pointed out in the discussion that rickets is practically nonexistent in the tropics where ultraviolet radiation is abundant in the sunlight but that other deficiency diseases which may be overcome by vitamins are especially prevalent in the tropics, and seem not to be affected by ultraviolet rays; beriberi and scurvy are examples. Sherman also brought out the fact that too long a radiation of cholesterol reduces the antirachitic activity but expressed the opinion that there was not much danger of this sort from over-exposure to sunlight. It has been found that activated cholesterol can be stored in the body. Eddy observed that if the solubility product of the calcium and phosphate ions is 40, regardless of the proportions of the two ions and if the p_H value is 7.35, calcium triphosphate is deposited but there are also colloidal and other problems to be considered. He remarked that inorganic phosphorus rises during the cure of rickets but other conditions also cause rise in the phosphorus; among these are cancer and the healing of ordinary wounds.

Experiments with other vitamins than the antirachitic and in other deficiency diseases than rickets seem to have met with no success. In this connection see: Powers, Park and Simmons;[63] Spinka,[64] Krizenecky,[65] Ishido.[66] A comment by Williams[67] on finding that foodstuffs may be rendered antirachitic by ultraviolet radiation is of significance. In his experiments the antineuritic factor was destroyed

[63] J. Biol. Chem. 1923, *55*, 575; Chem. Abs. 1923, *17*, 2130.
[64] Biochem. Z. 1924, *153*, 197.
[65] Arch. gesicht. Physiol. (Pflüger's) 1924, *204*, 467; Chem. Abs. 1924, *18*, 3209.
[66] Biochem. Z. 1923, *137*, 184; Chem. Abs. 1923, *17*, 3202.
[67] Science 1924, *60*, 499.

completely by radiation for a few hours of an aqueous yeast extract which was exposed to the rays of a quartz mercury arc lamp in a layer 2-3 millimeters deep. Both the irradiated and non-irradiated extracts were tested by feeding to pigeons otherwise maintained on a white rice diet. Experiments by Clark [68] on guinea pigs with different scorbutic diets showed that ultraviolet radiation is entirely ineffectual in preventing or postponing scurvy. With diets in which other factors, besides the scorbutic vitamin were lacking, ultraviolet hastened loss of weight and death from scurvy somewhat and prevented recovery after orange and cabbage were added to the diet. This, however, was not true when a diet lacking only in the antiscorbutic vitamin was used. Although water, on exposure to ultraviolet, is not activated, peanut oil similarly treated shows a definite growth-promoting action. Fuler, Widell and Erikson suggest that by virtue of the action of ultraviolet a factor related to *ID* (lipoid-soluble vitamin D), provisionally designated R, is formed. Since hardened peanut oil gives a negative result, it is concluded that the double bond is the grouping sensitive to irradiation. Oleic acid is faintly activated, stearic acid is not. The formation of vitamin A and *ID* in green plants is probably due to the double bond of the phytol. It was not found possible, however, to distinguish between the irradiated and non-irradiated oils by means of Drummond's vitamin A color reaction.[69]

[68] Science 1925, *61*, 45.
[69] Z. physiol. Chem. 1925, *144*, 123.

Chapter 15.

Miscellaneous Applications of Ultraviolet Rays.

Quick Ageing and Testing Methods.

Ultraviolet radiations form the basis of a host of interesting and novel processes. Some of these are still in a developmental or theoretical stage, while others are becoming recognized as aids to industrial progress. Many are of special or occasional interest only, such as the deciphering of damaged documents, or detection of frauds in paintings, while some are being adopted for such constantly important work as the testing of dyes for fastness and the artificial weathering of paints and varnishes. A third group embraces applications which, though possible, are of doubtful economic importance or feasibility.

Fastness of Dyes.

The employment of ultraviolet radiation has been strongly urged as the most reliable means of ascertaining the light fastness of dyes. Thus Pierce[1] highly recommends the use of ultraviolet for this purpose. He notes that some of the Government departments have recognized its value and the saving of time resulting from its employment. The opponents of ultraviolet rays as a substitute for sun and weather are prepared to show that many dyes vary in their fading by both methods and that no exact ratio is possible for all colors. These facts cannot be disputed but the same reasoning applied to sun and weather would lead to still worse confusion. The intensity of sunlight and the relative humidity, varying from day to day, make an exposure test a very irregular matter. It is difficult to tell whether the loss of color, which we call fading, is due so much to molecular disruption from the short rays of the sunlight as to a real bleaching action or oxidation. A comparison of a dry sample under glass also gives uncertain results as most of the active rays are kept out by the glass. When employing ultraviolet rays produced by an effective apparatus, the source of radiation, moisture and time can be exactly controlled and, having first exposed a standard, subsequent tests can be subjected to exactly the same conditions. Having once determined what is a satisfactory period of exposure this can be repeated with new samples at any time.

The lamp proper, recommended by Pierce, is a tube made of transparent quartz three-quarters of an inch by seven inches, with a well or depression at

[1] Chem. Engr. 1918, 97; Textile World Journal, Jan. 12, 1918.

one end, containing mercury, a high vacuum being necessary to satisfactory operation. The lamp is covered by a hood. The leading-in wires and anode are tungsten. This lamp is on a 200-volt circuit, but when in operation registers about 170 volts, 3½ amperes. There is a great increase in the number of short rays at this higher voltage and a lamp of this type will cause, in one second, an acute inflammation of the eyes lasting 3 days. Fifteen seconds exposure of the face, with the eyes protected by amber glasses, caused a reddening of the skin to develop several hours later, which was identical with sunburn.

The samples to be exposed are about 18 inches below the tube and must be protected by metal, as the rays penetrate slightly through cardboard. White wool is somewhat yellowed and the regular mixture for olive drab loses its mixed appearance during exposure as the white changes. From a number of tests it was computed that the exposure under the lamp noted had a value very close to eight times that of sunlight, or roughly one hour under the lamp equalled an average day's exposure. However, in such tests as have been stipulated by Government departments the orders have been for 48 hours exposure, which, Pierce observes, will fade the majority of dyestuffs. If the ultraviolet exposure is to be made an official test, it will be necessary to standardize it more closely. All lamps differ in power according to the voltage supplied and to the automatic resistance in their control. As the lamps age, the devitrification of the quartz, the deposit of tungsten oxides, and the loss of vacuum by leakage, cause a lessening of the radiation.[2] (See page 256.)

Gebhard[3] proposes using a cabinet with both an enclosed arc and a quartz mercury arc. The change of color, whether fading or change to another tint, is recorded by orthochromatic photography using a light filter of the same color as the original dyeings. Gebhard[4] has confirmed the theory[5] that the bleaching of dye solutions or of dyed tissues by light is due to the primary formation of a peroxide of the dye. The peroxide is best detected by acidified potassium iodide and starch, by alkaline potassium permanganate, or by diphenylamine and concentrated sulphuric acid. Chromic, molybdic and titanic acids do not indicate the presence of a peroxide, which fact furnishes one of Gebhard's several arguments against the theory of the primary formation of hydrogen peroxide. The rays which are most effective in the production of the peroxide are those complementary to the color of the dye. Blue, violet and ultraviolet rays exert a decomposing action on the peroxide, or occasion a transference of the active oxygen to unattacked molecules of the dye. Gebhard utilizes Mumm's theory of oxidation in the presence of water and shows by an electrolytic experiment that the perhydroxyions are instrumental in bleaching the dye.

[2] Flynn, Am. Dyestuff Rep. 1923, 12, 837, states that by starting a new 220-volt mercury lamp with 160 volt drop in the arc proper and increasing this voltage at the rate of 2 volts per 100 hours of operation during this period of mellowing, compensates almost exactly for the falling off in fading power of the tempered arc (see page 315) due to this aging. It is stated by Cady, Am. Dyestuff Rep. 1922, 11, 382, that the problem of standardizing methods for determining the fastness of dyes to light may be divided into two parts: standardizing the source of light and measuring and recording the amount of fading. The sun as a source of light is unsatisfactory because the intensity of the light and radiant energy received is constantly changing. Other conditions such as presence of moisture, fumes, etc., change during an exposure. Sun fading is too slow, especially in winter.

[3] Farben-Ztg. 1911, *22*, 6.

[4] Zeitsch. angew. Chem. 1910, *23*, 820; J. Chem. Soc. 1910, *98*, ii, 405.

[5] Zeitsch. angew. Chem. 1910, *22*, 2484.

Not all users of artificial light for fading tests urge the quartz mercury arc. A comparison made by Gordon [6] of the violet carbon arc, quartz mercury arcs, and Arizona and New Jersey sunlight as applied to testing dye fastness, shows that the mercury arcs are rapid in effects and satisfactory for a great majority of the dyes. However, he considers the results may be untrustworthy when compared to sunlight. The two mercury arcs were similar in character of action, but the violet carbon arc results are reported to compare closely to average sunlight; more closely than the Arizona and New Jersey sunlight compare with each other. It has been stated [7] that in general, the best means of determining the fastness to light of dyes is the violet carbon arc. The white-flame carbon arc has given rather better results in some cases but is only half as rapid while both of these are claimed by their supporters to be superior in constancy to the mercury arc. Mott and Bedford [8] consider the flame arc [9] to be better for testing the fastness of dyes, than the quartz mercury lamp. For equal line energy, the effect on solio paper of the white flame arc was five to six times better than the efficiency of a 110-volt quartz mercury lamp operating at 4 amperes and 60 arc volts.

Scheurer [10] also has compared the action of sunlight with ultraviolet radiation produced by the quartz mercury arc on dyes. When using ultraviolet the dyes were protected against the ozone formed. Benzo colors were hardly faded by sunlight, but in 24 hours by the quartz mercury arc they were materially changed. Indigo resisted the mercury arc better than it did sunlight.

After an extended study of the action of the light of the mercury arc on dyes and fibres Harrison [11] agrees with Walther and Scheurer that light from the mercury arc lamp does not act relatively the same as sunlight on all colors and also reports that the mercury arc lamp of high intensity does not act relatively the same as that of low intensity. Cellulose is decomposed by the action of the rays and air with formation of reducing substances, and in a vacuum under the influence of the mercury arc cellulose acts as a reducing agent, and reduces flavanthrene and many direct colors, the cellulose itself being oxidized. The reducing power of cellulose increases with the intensity of the mercury arc. In a vacuum, under the influence of sunlight, cellulose has little reducing power, but hydrocellulose and oxycellulose reduce flavanthrene and diamine sky blue. This explains why direct colors do not fade in a vacuum under the influence of sunlight. Most colors do not fade in

[6] Textile Colorist 1921, *43*, 29.

[7] J. Soc. Chem. Ind. 1921, *40*, 149R.

[8] J. Ind. Eng. Chem. 1916, *8*, 1029. Comparative tests of the violet carbon arc, the mercury-vapor arc and sunlight are reported by the sub-committee on light fastness, Cady, Proc. Am. Assoc. Textile Chem. Colorists 1925, 42; Am. Dyestuff Rept. *14*, 58; Chem. Abs. *18*, 906. The object of the committee is to find a substitute for sunlight whose fading action will have (1) speed, (2) close similarity to the sun's action, (3) a capacity for exact reproduction at different times and in different places.

[9] See Chap. 2.

[10] Bull. soc. ind. Mulhouse, 1911, *80*, 324.

[11] J. Soc. Dyers and Colourists 1912, *28*, 225.

the absence of fibre and air; direct colors do not fade in absence of fibre; basic colors do not fade in absence of air. Basic colors usually fade by oxidation, but may fade by reduction under certain conditions. Under the influence of the mercury arc, wool is not as powerful a reducing agent as cellulose. Flynn [12] examined and interpreted Harrison's results, made further studies of the applicability of the mercury arc in testing dye fastness and also experimented with means of tempering the light with crown glass to approximate sunlight more closely. Figure 76 shows Flynn's interpretation of Harrison's results

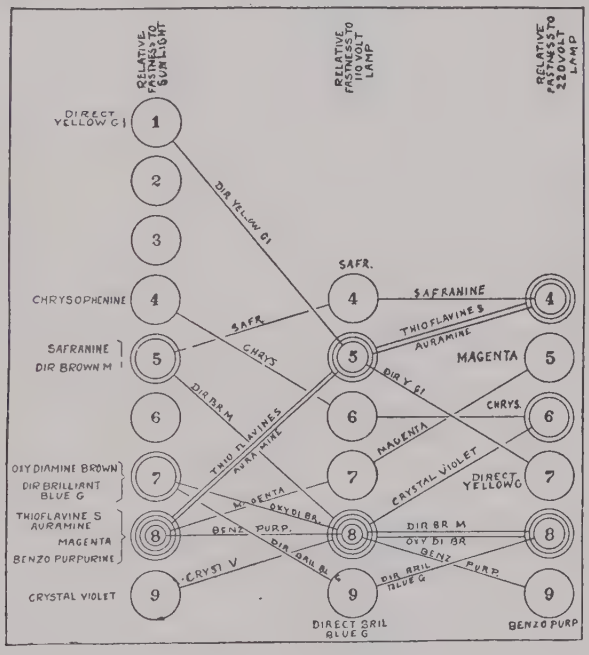


FIG. 76.

regarding the relative fastness of various dyes when exposed to sunlight, 110-volt and 220-volt quartz mercury vapor lamps.

Figure 77 illustrates the relative fading of dyes on cotton when exposed to sunlight, direct quartz mercury arc and the arc tempered by passing through 1.25 millimeters of crown glass. The dyes are represented as rectangular strips, the degree of fading being represented by a part of the strip cut out. The sunlight fading is at one end and the tempered mercury light fading at the other. The intervening fadings represent the effect of one-half hour and one hour exposure by direct mercury light and shows the reversal of relative fastness between the direct and basic dyes when exposed to the strong untempered mercury arc.

[12] Textile World 1923, *53*, 25.

This reversal is considered to be due to the fact that direct dyes fade by reduction, which is accelerated by the action of ultraviolet rays on cellulose, while basic dyes fade by oxidation.[13] Silk and wool appear to have less reducing action than cotton under the influence of the rays of the mercury arc.

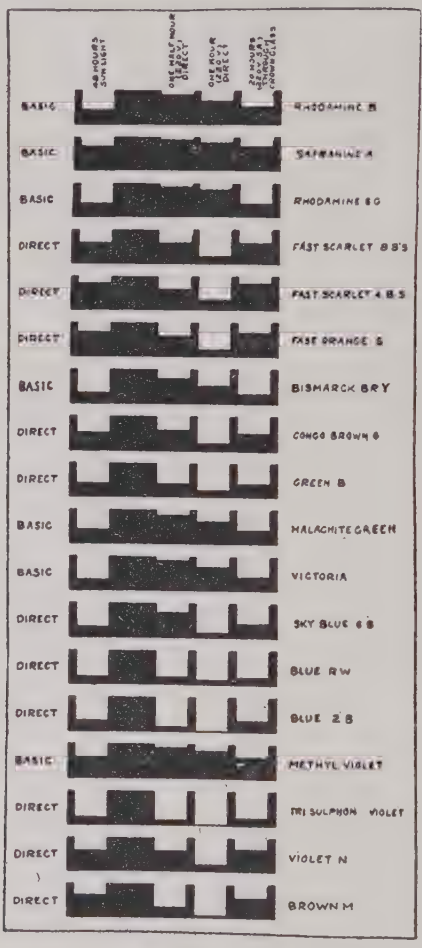


FIG. 77.

Heermann [14] proposes to classify "dye and textile fibre" systems into four groups according to their susceptibility to light of various wavelengths. The behavior has been examined with reference to sunlight transmitted through glass (350-3000 μμ, 3500-30000 Å), direct sunlight

[13] See also Am. Dyestuff Rep. 1923, *12*, 837.
[14] Chem.-Ztg. 1924, *48*, 813 and 834.

(300-4000 μμ, 3000-40000 Å) and light such as that obtained by means of a mercury vapor lamp (185-600 μμ, 1850-6000 Å). These classes, termed "micro-," "macro-," "homo-," and "meso-tropic," are, respectively, most susceptible to light of short wave-length, long wave-length, all wave-lengths, and to the ultraviolet rays present in the sunlight. Although fading of dyed fabrics is induced in most cases by that portion of the incident light which has a wave-length less than 300 μμ (3000 Å) there are several instances of dyeings which are more affected by longer wave-lengths. Thus, auramine, notoriously not fast to sunlight, resists short ultraviolet rays rather well. By exposing dyeings made up according to the standards of the German Fastness Commission [15] to sunlight filtered through glass, and to the radiation of a quartz tube mercury arc, it was found that six of the cotton types were faded almost entirely by rays of less than 300 μμ (3000 Å) wave-length, but that two were also faded by visible light. Similarly with the wool types, three were faded exclusively by the short ultraviolet wave-lengths, one was sensitive to visible light as well, and four were most affected by rays of 300-400 μμ (3000-4000 Å) wave-length. None of the dyeings tested faded exclusively in visible light. These results have brought forth the criticism that the mercury arc should not be used for dye testing as some of the injurious wave-lengths are not present in the mercury spectrum.[16]

An apparatus for dye or paint testing now on the market [17] consists of a vertical quartz mercury arc lamp disposed in the center of a circular cabinet, the walls of which consist of removable panels to which the samples are attached. (See Figure 78).

Testing Inks.

Proposals to employ ultraviolet radiation for testing inks have followed this method of testing in the dye industry. Rupert [18] discusses the relation of the composition of ink to its color, permanence, stability, and non-corrosiveness. Streaks are formed by allowing the ink to flow from a small pipette down paper supported on an inclined surface. The fluidity and penetration are noted and observations made of the temporary color and that exhibited after exposure for seven days to diffused light. The permanence is measured by exposure for at least two weeks to sunlight or for a shorter period to ultraviolet; strips are also exposed to the weather, and immersed in water.

In the testing of inks the Bureau of Standards [19] recommends ex-

[15] Chem. Abs. *11*, 2963.

[16] Cunliffe, J. Text. Inst. 1924, *15*, 173, reviews the literature on the action of light on dyes applied to cotton fabrics considering the following topics: comparative tests of fading, absolute measurement of fading, sources of light, influence of atmosphere on fading, influence of color of light on fading, relation between active rays and absorption spectra of dyestuffs, influence of temperature on fading, influence of added substances and the protection of fabrics from fading, theories of fading action, and relation between constitution and fading.

[17] Cooper Hewitt Electric Co.

[18] Ind. Eng. Chem. 1923, *15*, 489; J. S. C. I. 1923, *42*, 612A.

[19] Circular 95, June 28, 1920.

posure of impressions of the ink on paper to the action of ultraviolet rays for 48 hours. In carrying out this test, streaks of the inks under examination are produced on a sheet of paper along with a streak made with standard ink. The paper containing the streaks is then exposed to rays of ultraviolet for varying periods, generally about 48 hours, and the relative effect noted. The method is therefore simply a comparison test with standard material.[20]

Drying of Oils.

The acceleration of the drying of siccative oils by ultraviolet rays has not been overlooked and certain applications of a commercial char-

Courtesy Cooper-Hewitt Electric Company.

FIG. 78.—Apparatus for Dye or Paint Testing.

acter have been proposed which utilize ultraviolet. In studying the phenomena of drying linseed oil Genthe [20a] made use of the ultraviolet radiation. The oil was exposed on filter paper to an atmosphere of oxygen in a quartz flask. A series of these flasks were exposed to the Uviol lamp, during which exposure the absorption of oxygen was measured. Caustic potash was placed in the bottom of the vessel to absorb volatile acid products. No formation of ozone was noted. During the first 2 hours the absorption of oxygen was slight. In the third hour the absorption became very rapid, gradually diminishing in rate during subsequent hours of insolation. In the laboratory of the senior author

[20] Private communication from Percy H. Walker, Bureau of Standards.
[20a] Z. angew. Chem. 1906, 2090.

a large number of samples of varnishes of various grades have been exposed to ultraviolet rays. The behavior of varnishes varies greatly, depending on the composition. Some samples are bleached, others are darkened and still others are very little altered in color. In some cases the varnish was floated on a layer of water to prevent overheating. In other cases the samples were enclosed with the lamp in a chamber and inert gases or steam passed through the chamber during the treatment. There did not appear to be any great difference in results when taking these precautions as compared with samples exposed to the normal atmosphere. Samples of linseed oil were also exposed under the same conditions. In most cases the oil was considerably bleached and with raw oil, practically no skin was formed over the top. With boiled oil, a film was formed on exposing linseed oil to the action of the rays for 6 hours, when free access of air was allowed. In one case where the oil was exposed in a thin layer over water, the oil became turbid and apparently a very stable emulsion was formed. In another case a sample of raw oil was exposed for 7 hours in a closed chamber in an atmosphere of steam. The oil, which was quite dark at the beginning, was bleached to a light straw color.[20b] An apparatus for oxidizing oils is described by Schofield.[21] The oil, such as linseed oil, is sprayed through a chamber illuminated by a high tension electrical discharge. Purified and dried air is also supplied to the chamber, under pressure and at a temperature of about 250° C.

The influence of light of different wave-lengths on the drying of varnishes has been investigated by Wolff,[22] who concludes that light of short wave-length induces a rapid oxidation on the surface and also polymerisation in the inner layers, both effects proceeding at the same rate, while light of long wave-length of low actinic value results in a greater rapidity of oxidation taking place in the surface than polymerisation in the inner zone. Alterations in volume in the different zones with consequent production of shrivelling thus result from exposure to yellow, orange, or red light during drying. Wolff's conclusions are criticized by Ragg,[23] who points out that a higher rate of oxidation with a reduced rate of polymerization would induce cracking in contradistinction to shrivelling. He offers the alternative hypothesis of the filtration of the ultraviolet rays in the surface, thereby transmitting only light of low actinic value to the inner zones, but while pointing out the necessity of consideration of possible thermal effects, does not make himself clear as to his interpretation of the mechanism of shrivelling. Wolff,[24] in replying to Ragg's criticisms, remarks that red light does not actually accelerate the rate of oxidation of varnish but induces a slight retardation of surface oxidation while considerably retarding polymerisation in the inner layer; light of short wave-length on the other hand allows oxidation and polymerisation to proceed at

[20b] Ellis and Wells, Chemical Engineer, 1918, 116.
[21] British Patent 227,212, Oct. 16, 1923; J. S. C. I. 1925, 180.
[22] Farben-Zeit. 1919, *24*, 1119; J. Chem. Soc. 1919, *115*, 915A.
[23] Farben-Zeit. 1919, *24*, 1308; J. Chem. Soc. 1919, *115*, 915 A.
[24] Farben-Zeit. 1919, *24*, 1389.

nearly equal rates. A later contribution to the discussion by Vollmann [25] suggests that red rays act exclusively by development of heat in both inner and outer layers, this effect influencing the polymerisation of the inner layers. The cause of shrivelling in varnish and oil films needs more investigation particularly in respect to the special occurrence of this phenomenon in products rich in tung oil.[25a]

From experiments on the influence of colored and ultraviolet rays on the drying of linseed oil and varnish, Gardner and Parks [26] found that when direct sunlight, both pure and filtered through plain, ground, red, amber, blue, or green glass, was employed as illuminant no appreciable differences in the times of drying of a film of raw, unsiccatised linseed oil exposed to the air were noted. All conditions resulted in greatly accelerated drying over that of a film exposed in the dark. When, however, diffused daylight under the above-mentioned conditions was employed as the source of light, the following times of drying were noted: pure unfiltered light, 4 days; amber glass, 11 days; blue glass, 13 days; darkness, plain glass, ground glass, red glass and green glass, 14 days. The effect of heavily siccatising the oil was to cause the films under all conditions, including exposure in darkness, to dry in 6 hours. Previous exposure of a film of raw unsiccatised linseed oil to the ultraviolet rays of an iron arc for 30 minutes produced a great acceleration in drying, which was shown to be independent of the heat resulting from the irradiation. When the ultraviolet rays were screened through red glass, the accelerating effect was lost.

Patent Leather.

In drying japanned or "patent" leather by the action of ultraviolet rays one process is carried out in an atmosphere containing ammonia derivatives, nitrogen, hydrogen or other neutral gases,[27] or in an exhausted chamber. In addition to the gases above mentioned, marsh gas, coal gas, carbon dioxide, carbon monoxide, or other gas that does not give off oxygen under the action of the rays may be used. The leather is carried on frames in the chamber, quartz lamps being arranged between the frames.[28] Lumbard [29] discusses the use of ultraviolet rays in the manufacture of patent leather. It is claimed that the exposure of the varnished surfaces to the action of mercury vapor lamps gives the same result in one and one-half hours as is obtained by several days' exposure to sunlight. Lumbard claims that better results are

[25] Farben-Zeit. 1919, *24*, 1427.

[25a] Tung oil, 90 per cent of which consists of the glyceride of α elæostearic (α elæomargaric) acid is converted, by exposure for 48 hours to the radiation from a mercury vapor lamp, into glyceryl tri-β-elæostearate. Böeseken and Ravenswaay, Rec. trav. chim. 1925, *44*, 241.

[26] Circ. 172, U. S. Paint Manuf. Assoc., March, 1923.

[27] Heyl, British Patent 113,622, Feb. 21, 1918; Swiss Patent 76,436, Dec. 17, 1917; British Patent 113,620, Feb. 20, 1918.

[28] See also Swiss Patents Nos. 77,117 and 77,378; Holland Patent 1,970; Danish Patents 22,258 and 22,269; Hintz, J. Soc. Chem. Ind. 1918, *37*, 709A; Chem. Abs. 1918, *12*, 1935; U. S. Patent 1,269,931, June 18, 1918.

[29] J. Am. Leather Chem. Assn. 1915, 84.

obtained if the extreme ultraviolet rays are filtered out. An apparatus for the treatment of patent leather with ultraviolet rays is recommended by Priest,[30] who states that after leather is coated with the linseed oil varnish mixture customarily employed, the stock is exposed to the direct rays of the sun for a period of 8 or 10 hours. The drying takes place best in clear, cool weather, and is greatly retarded by a humid atmosphere.[30a] In order to dry the leather rapidly, Priest uses ultraviolet rays which accomplish the drying operation in from 2 to 6 hours. A frame arranged on bearings so that it may be revolved serves as a support for the hides which are to have their varnished surfaces exposed to the direct action of the ultraviolet rays. A series of quartz lamps are arranged vertically in the center of the revolving frame at the bottom. The action of the ultraviolet may also be supplemented, according to Priest, by the use of ozone. The surface of varnished leather Stoeckly finds can be effectively dried [31] by means of ultraviolet rays produced by a high frequency electric spark discharging 30-60 times per second, each spark consuming about 0.7 kilowatt.[32]

Durability of Coatings.

Accelerated weathering tests for paint films have been carried out by Nelson [33] in a wooden exposure tank surrounded by an insulated air space and lined with galvanized iron. Effects of sunlight, rain, and mist have been simulated by a quartz mercury arc lamp of 30 inches effective length, a revolving spray, and a water atomizer respectively, together with a variable speed electric fan serving to cool the arc and maintain a uniform temperature. See Figure 79.

A cycle of exposure for 24 hours to the rays of the arc at a temperature of 50°-60° C., followed by cooling and exposure to the water spray for a further 24 hours at 5°-10° C. was chosen as representing actual service conditions. Exposures were made at a distance of 28 inches from the source of the rays, investigation proving that the useful rays of destructive effect had a wave-length in the neighborhood of 300 μμ (3000 Å). On an average, comparable results were obtained in as many days in the apparatus as in months under service conditions. The following results were obtained on a series of paints, the figures referring to the number of days necessary for the complete loss of gloss, and initial chalking, respectively: 100 per cent lead-free zinc oxide, 14, 16; 100 per cent leaded (35 per cent) zinc oxide, 9, 12; 100 per cent light-resistant lithopone, 4, 6; 100 per cent basic lead carbonate, 3, 5; 100 per cent "Titanox," 2, 4; a mixture of 40 per cent zinc oxide, 40 per cent lithopone, 20 per cent whiting, 9, 11. The effect of periodic saturation and maintenance of a saturated atmosphere during exposure is to accelerate both complete loss

[30] U. S. Patent 1,262,977, Apr. 16, 1918; J. Soc. Chem. Ind. 1918, 343A.

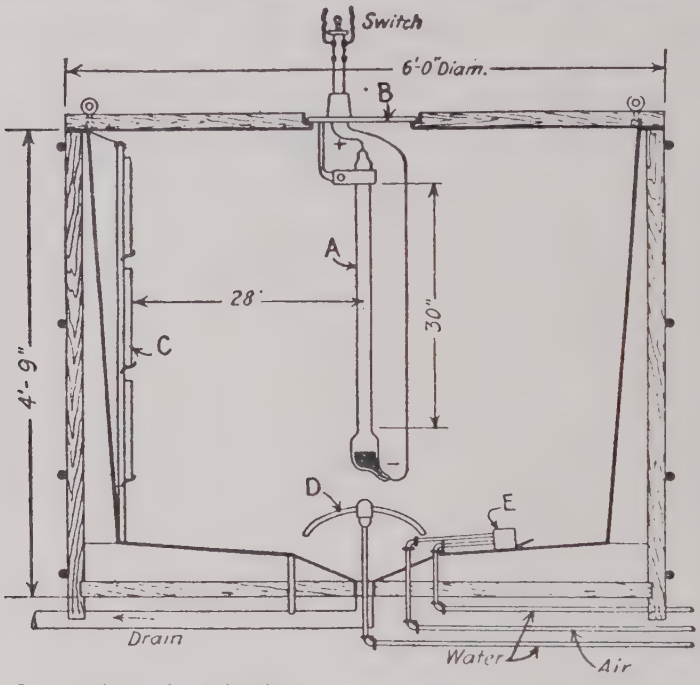
[30a] Genthe, U. S. Pat. 1,095,498, May 5, 1914, dries japanned or varnished leather by treating it with dried air in a closed chamber and exposing to light rich in ultraviolet rays.

[31] British Patent 149,334, July, 1920.

[32] Leather may be subjected to ultraviolet rays prior to being enamelled or treated. Dinsley and Pulman, British Patent 190,781, Sept. 23, 1921; J. Soc. Chem. Ind. 1923, *42*, 193A.

[33] Am. Soc. Test. Materials 1922, *22*, II, 485. The testing of automobile body finishes through the aid of ultraviolet radiation is described by Carver, Automotive Industries, 1924, 1011. Note Green, Microscopy of Paint and Rubber Pigments, Chem. and Met. Eng. 1923, *28*, 53.

of gloss and initial chalking by 50 per cent, a fact attributed to the activity of dissolved oxygen in an ionised condition. Freezing of a saturated film materially promotes the formation of removable "chalk" most probably due to the formation of ice within the film. Neither flaking nor checking has been reproduced in any of the tests. Cracking, rapidly followed by scaling and peeling, is pro-



Courtesy Automotive Industries.

FIG. 79.—An exposure tank constructed by Nelson which facilitates the maintenance of diverse "weathering" conditions. This tank is of wood with an insulating space and galvanized iron lining. The cover is provided with a 10 inch opening, which receives a removable collar B supporting a quartz mercury arc A of 30 in. effective lighting length. The test panels C are supported by nails on removable racks provided with sheet zinc water drains. Water simulating a beating rain is provided by a revolving spray D, and fine fog or mist by the atomizer E. An ordinary variable speed electric fan serves to cool the mercury arc and maintain uniform temperature. The arc is used on a 220-240 volt direct current normally drawing 6-7 amp. when the atmosphere within the exposure tank is maintained at 50-60° C.

duced by periodic exposures to temperatures considerably below freezing-point, and is reproducible by exposures of equal alternate intervals to radiation, low temperature, and water-spray for a period of 100 days, equivalent to 14-15 months' exposure to the weather. Lack of adherence is a fault more strictly connected with the method of application of the paint, but can be brought about by exposure at 50°-60° C. to the mercury arc. Of commercial paints intended for use as protective coatings for iron, both a 100 per cent red lead paint and the mixture of 85 per cent ferric oxide with 15 per cent zinc oxide showed outstanding merit in maintaining gloss and inhibiting the formation of rust as compared with iron oxide paints containing various fillers, and a zinc oxide sublimed lead paint also containing a filler. While a certain light-resistant

lithopone maintained its whiteness over a period of three years on exterior exposure, the effect of the ultraviolet radiations was to discolor both this product and white lead in a short time.

The effect on paint films of the application of fixed loads in regard to elongation and time required to break the stressed films, and the effect of the rate of elongation on the ultimate distensibility of the films has been studied by Nelson and Rundle.[34] Films exposed to ultraviolet rays increase in tensile strength and decrease in extensibility, but this effect is less pronounced with films containing zinc oxide which is opaque to ultraviolet radiations, than with films containing basic car-

FIG. 80.—Freshly Oxidized Linseed Oil Film Before Exposure to Ultraviolet. (Dark Spots are Dust Particles.)

FIG. 81.—Film After 13 Hours' Exposure to Ultraviolet Rays.[35a]

bonate white lead which is more transparent. The hardening, and subsequent disintegration of the surface of a linseed oil binder through reactions induced by ultraviolet radiations must be recognized as a fundamental cause for the failure of paints by chalking. Visible evidence of chalking may be hastened by temperature expansion and contraction effects, but chalking may be reproduced on pigments such as basic carbonate white lead by ultraviolet exposure alone without introducing any temperature or moisture variations.

Pfund[35] reports determinations of coefficients of diffuse reflections from dry pigment surfaces made by calculation from photographic records. The source of incident light was a small quartz mercury lamp which rayed the pigment surface. The diffusely reflected light was allowed to enter the slit of a small concave-grating spectograph, and then

[34] Proc. Am. Soc. Testing Materials 1923, *23*, II, 356.
[35] Proc. Am. Soc. Testing Materials 1923, *23*, II, 369.
[35a] By Nelson. Courtesy of Research Division, New Jersey Zinc Company. The films were subjected to an extension of ten per cent before the photomicrographs were made.

to fall on the photographic plate. When light falls on a thick layer of fine particles, it penetrates a large number of particles before being returned, so that the reflection coefficients give roughly qualitative results for the opacities of the pigments examined. Zinc oxide becomes practically opaque near 360 μμ (3600 Å); basic carbonate white lead is by far the most transparent pigment examined. Titanox, timonox, lithopone, and sublimed white lead fall between these limits. Powdered sulfur is very opaque. Fumed magnesia has constant reflecting power throughout the ultraviolet spectrum. It is not possible to obtain accurate values for ultraviolet transmission through actual paint films because of the diffuse transmission, but qualitative results on pigment-linseed oil mixtures with a volume ratio of pigment to vehicle of 1:60 lms 0.065 millimeter thick were made. Linseed oil is opaque to wave-lengths less than 290 μμ (2900 Å), but determination of the decreased transmission due to the pigment placed the transparencies of the pigments in the same relative position as the determination of diffuse reflection coefficients. The transmission of the inert pigments is very high and is nearly non-selective. Since ultraviolet radiation is one of the most serious causes of the decomposition of the oil vehicle in paint films, it is a desirable function of the pigment to absorb the harmful radiations. This is accomplished most effectively by sulfur and zinc oxide and least effectively by the inerts. By projecting the entire spectrum of an iron arc upon a lithopone water paste, it was found that wave-lengths greater than 320 μμ (3200 Å) show very little darkening effect. Determination of a relation between darkening and the wave-length of incident light was accomplished by eliminating the variations in energy from light of different wave-lengths by the use of a quartz monochromator and the so-called method of "equal energies." The resultant curve shows that the sensitivity of lithopone is essentially zero in the visible spectrum, and rises to a high value in the ultraviolet near 290 μμ (2900 Å) and thereafter remains practically constant. The visible solar spectrum stops at nearly the same wave-length at which lithopone is most light-sensitive. All lithopones exhibit the same general type of sensitivity curve. A new process lithopone showed a light stability of 135 seconds exposure, compared to four seconds exposure for an old process lithopone. Qualitative results on the bleaching action of light on yellowed paint films show that pronounced bleaching takes place at much greater wave-lengths—in fact up into the visible spectrum —320 μμ (3200 Å) or less, than is required to produce decided deterioration of paints and darkening of lithopones. If two similar zinc plates coated with lithopone are immersed in a weak electrolyte, an electric current is set up when one of the surfaces is irradiated. (See page 139.)

The transmission and reflection of ultraviolet radiation by paint films was studied by Hallett.[36] The light from a quartz mercury lamp after passing through a suitable glass filter to remove practically all of the visible spectrum, passed through a quartz lens on to the painted surface from where it was either reflected or transmitted to sensitized paper. The paper was developed under standard conditions and the degree of

[36] Proc. Am. Soc. Testing Materials 1923, *23*, II, 379; Chem. and Met. Eng. 1923, *29*, 64.

black determined by measurement with a Howland color photometer, and calculated to the "Artura scale," considering the unexposed paper as zero and the completely exposed paper as 100 per cent black. Complete details of the method of standardizing the apparatus are given. Transmission and reflection measurements on paints, made with various pigments all in the same volume relation to the vehicle, were made. The values in per cent for reflection, transmission and absorption, respectively, by paints containing the following pigments are: Basic

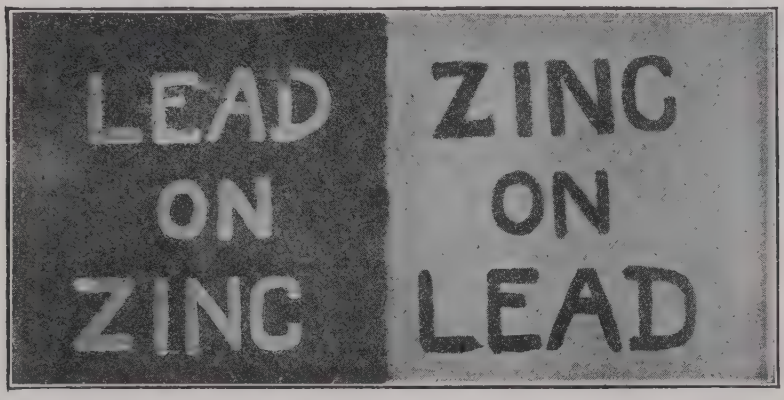


FIG. 82.—Photograph Taken by Reflected Light Radiations from the Near Ultraviolet, Illustrating Differences in Transmission by Two Pigments.[36a]

carbonate white lead 42, 4, 54; zinc oxide 0, 0, 100; basic sulfate white lead 3, 0, 97; titanox 16, 0, 84; lithopone 36, 1, 63; red lead 1, 0, 99; iron oxide 1, 0, 99; lampblack 2, 0, 98.

Gardner and Holdt [37] state that the sensitiveness to light of lithopone may be determined by exposure of the pigment to sunlight, or for an accelerated test, to the rays of a mercury or iron arc. When the mercury arc is used, the pigment is exposed as a dried oil paint film on a palette submerged in a shallow layer of water, in order to reproduce the condition of constant humidity for the test, the influence of moisture on the darkening of lithopone being very marked. The test should be carried out on the pigment ground in the vehicle with which it is eventually destined to be used; the use of water or glycerol as vehicle does not necessarily furnish results comparable with those in oil or varnish media. The acid value of the oil medium used has a marked effect on the darkening of lithopone, an increasing acid value in a series of alkali-refined linseed oils, and also tung oils, substantially diminishing but not entirely inhibiting darkening of the pigment. When employing the

[36a] To the eye the lettering and background are white and quite indistinguishable. Photographed in the rays of an iron arc (ultraviolet range 3800-3100 Å) one pigment, zinc oxide, did not reflect any radiations to activate the plate. The other pigment, basic carbonate white lead reflected the radiation and hence appears of normal white color. By Nelson and Rundle, Proc. Am. Soc. Test. Mat. 1923, *23*, II, 362. Courtesy of Research Division, New Jersey Zinc Company.

[37] U. S. Paint Mfg. Assoc. Circ. 194, January, 1924. See Chapter 7.

rays from an iron arc as a source of light, advantage may be taken of the effect of water in accelerating the test by exposing the lithopone (ground to a paste in water) behind a quartz glass slide, the adhering paste being backed with a slide of ordinary glass to retard evaporation. When employing sunlight as an illuminant, it is preferable to expose the pigment ground to a paste in water between thin microscope slides, and to evaluate the degree of darkening against standards. Many pigments other than lithopone, even some of the so-called inert pigments, darken or show a slight graying on exposure to ultraviolet rays.

The one salutary effect of light on paints is its bleaching action on yellowed surfaces. While no quantitative data have been gathered on

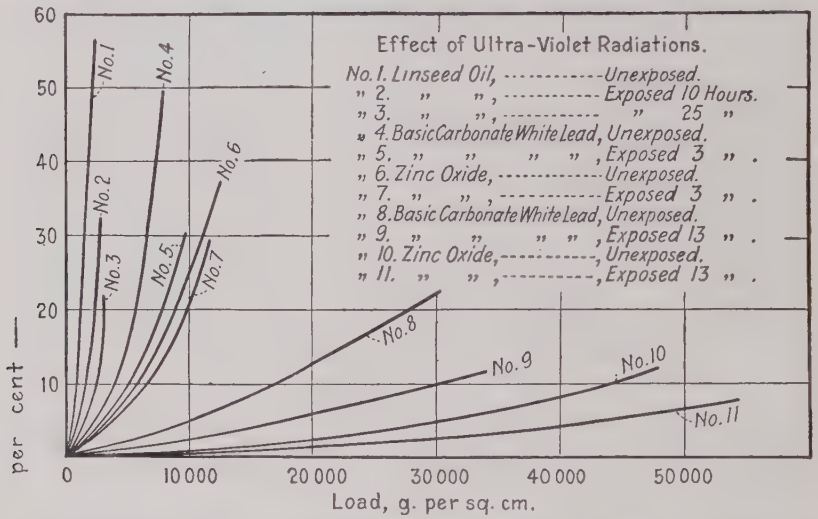


FIG. 83.—Results of stress-strain tests, conducted by Nelson and Rundle, on paint films, showing elongation in per cent, before and after exposure to ultraviolet radiation.

the bleaching effects of the different spectral regions, some qualitative results have been obtained by Pfund [37a] through exposing a badly yellowed paint film (linseed oil) to sunlight. Adjacent patches of the film were covered with the screens described below. The second column indicates the shortest wave-length reaching the film.

	WAVE-LENGTH	REMARKS
(*a*) No screen	2900 Å	Vigorous bleaching
(*b*) Quartz	2900 Å	Vigorous bleaching, same as (*a*)
(*c*) Glass plate	3200 Å	Vigorous bleaching, same as (*a*)
(*d*) Crookes' glass..	3600 Å	Vigorous bleaching, slightly less than (*a*)
(*e*) Noviol (yellow) glass	4900 Å	Bleaching, pronouncedly less than (*d*)
(*e*) Ruby glass	6000 Å	No bleaching

[37a] Proc. Am. Soc. Testing Materials 1923, *23*, ii, 377.

From this table it is seen that, whereas light of wave-length 3200 Å or less is required to produce pronounced deterioration of paints and darkening of lithopones, the beneficial bleaching action extends to much greater wave-lengths—in fact, up into the visible spectrum.

A revolving-type accelerated testing device used by Gardner [37b] exposes painted panels to four cycles: heat, cold, rain and ultraviolet radiation.

During the past few years the ultraviolet lamp has been used extensively for the testing of nitrocellulose lacquers, lacquer enamels and other finishes. Although it is possible to obtain the breakdown of finishes by this method, Mougey [37c] has not been able to find a direct relationship between ultraviolet ray tests and service tests when different types of materials are compared, and variations in the application of the ultraviolet ray tests make such great differences that it is very difficult to make predictions as to the service durability of two finishes, even though they are of the same type. For example, the first method used to test finishes by the ultraviolet rays was simply to expose the test panels under the lamp. In the case of tests made by Mougey on black baking fender enamel, the panels failed on the test racks on the roof before they did under the ultraviolet radiation.

The panels were then soaked in water overnight and exposed to the ultraviolet rays during the day. This gave failures in a very few days, but unless care was taken to dry the panels of surface water the results were of no value, failure occurring in a few minutes at the areas where surface water lay on the panels. Finishing varnishes subjected to this test usually failed in one cycle, with no relation between this test and the durability of the varnish. It was apparent that this test favored hard-drying finishes, and the test was then modified to use a rotating wheel type of exposure apparatus. The panels were mounted on the rim of the wheel, and the latter, half immersed in water, was rotated under the ultraviolet lamp at the rate of two revolutions per hour, thus soaking the finish, allowing time for drainage and evaporation of the surface moisture, and then exposing the panel to the rays. A nitrocellulose lacquer enamel [37d] which would withstand exposure on the roof test racks over 2 years, would fail in 2 days, while a finishing varnish having a life of 3 months on the roof test would stand 2 or 3 weeks under this test. Apparently, there was no connection between the results of the test and the life of finishing materials on the roof test racks.

A method which has given much better results and which was finally adopted by Mougey involves continuous rotation of the wheel day and night but with the lamp turned on only during the day.

Treatment of Various Oils.

In the field of non-drying oils ultraviolet radiation has found some applications. Wall [38] subjected cacao oil to the action of ultraviolet rays

[37b] Paint Manufacturers Assoc. of U. S. Circ. 226, 1925, 179.
[37c] Ind. & Eng. Chem. 1925, *17*, 412.
[37d] Known as Duco.
[38] Wall, U. S. Patent 1,386,476.

to destroy its objectionable taste and odor. Putland [39] observed a more rapid bleaching of vegetable oils in the light from Mazda lamps than in sunlight. Ultraviolet from a quartz mercury vapor lamp, however, darkened instead of bleaching both cottonseed and soy-bean oils. Crude cottonseed oils, 1 inch in depth, exposed in a tin tray at a temperature of 27° C. to the mercury vapor light darkened from 35 yellow, 7.9 red (Lovibond scale) in 8 hours to 35 yellow, 8.3 red. Similarly a bleached cottonseed oil in 10 hours changed from 20 yellow, 2.1 red to 20 yellow, 3.0 orange. The bleaching of oils, fats, waxes and resins by the joint action of oxygen and rays of short wave-length is proposed by Genthe.[39a] The oil, fat or other substance is heated to 70-90° C. and is then subjected to the action of rays from mercury vapor lamps immersed in the substance which is being treated. At the same time air is blown through the hollow arms of a stirrer which serves for agitation. Genthe claims that 1000 kilos of linseed oil can be bleached with an expenditure of 60 kilowatt-hours for current, 30 h.p. hours and 1500 cubic meters of compressed air. In order to ascertain the liability of oils to stain textile fabrics Gray [39b] proposes to expose pieces of tape, treated with the oils, to the light from a Cooper-Hewitt quartz mercury arc lamp, using a standard oil for purposes of comparison. A half hour exposure at a distance of 6 inches from the lamp, was found to be sufficient to develop a stain with oils likely to discolor fabrics. Lesure [39c] has observed that exposure of olive oil for an hour to ultraviolet radiation caused an increase of more than 5 per cent in the acidity.

In the laboratory of the senior author numerous experiments have been made to test the effect of ultraviolet on various oils, resins, etc., especially in regard to the bleaching action and polymerization. A résumé of some of these tests follows. The lamp used was a Cooper-Hewitt quartz mercury arc, using 150 volts at 3½ amperes.[39d]

The following oils, among others, were subjected to the action of ultraviolet rays to ascertain whether any bleaching effect was exerted: Crude cottonseed oil, linseed oil, crude whale oil (No. 3) and lubricating oil of medium body and strongly fluorescent. The oils were exposed in shallow pans in layers about three-sixteenths of an inch thick and spaced about 11 inches from the lamp. After 3 hours' exposure the linseed oil had a very heavy film over the surface. The cottonseed and whale oils had slight films, while the surface of the lubricating oil was apparently unaltered. After 6 hours' exposure the cottonseed oil had greatly increased in viscosity, the linseed and whale oil had commenced to gelatinize and the lubricating oil had become slightly darker. At the end of 13½ hours the cottonseed oil had gelatinized and was slightly bleached. The linseed oil had become a stiff jelly and the linseed odor was diminished. The color was apparently unchanged. The whale oil was considerably deodorized and slightly bleached. The lubricating oil had become somewhat darker, but the fluorescence had completely disappeared.[39e]

On exposure of whale oil in layers about three-sixteenths of an inch in thickness and placed 4 inches from the lamp for 10 hours, a dark amber-

[39] Cotton Oil Press 1923, 7, No. 7, 36.

[39a] Ger. Pat. 223,419, Aug. 24, 1907; J. Soc. Chem. Ind. 1910, 1168; Chem. Abs. 1910, 3146.

[39b] Oil, Paint & Drug Reporter, Aug. 9, 1915.

[39c] J. Pharm. Chim. 7, 1575.

[39d] Note U. S. Patents, 1,179,414 and 1,180,025.

[39e] See Ellis, U. S. patent 1,089,359, Mar. 3, 1914.

colored jelly resulted, the odor of which was very faint as compared with the original oil. Crude cottonseed oil exposed for 7 hours at a distance of 6 inches from the lamp gave a stiff amber-colored jelly. The jelly was considerably lighter than the original oil and the iodine value had fallen to 56. China wood oil treated under the same conditions gave a hard jelly which on exposure for an hour or more became so brittle that it could be easily pulverized. The powdered product was almost white. The iodine value of this product was 93. Linseed oil treated in the same manner gave a resilient translucent jelly of practically the same color as the original oil. A highly refined cottonseed oil placed 4 inches from the lamp for 13 hours gave an amber colored jelly of practically the same color and consistency as the crude cotton oil. Castor oil when exposed at a distance of 3 inches from the lamp for 10½ hours gave a product which was identical in appearance and odor to that obtained from cottonseed oil. Red oil (crude oleic acid) when exposed for 14 hours at a distance of 4 inches gave an entirely different product from the other oils. It was noted that fumes were given off at a very low temperature. At 85° C. slight fuming was noticed. At 110° C. copious fumes were given off. The manner in which this oil thickens suggests crystallization, while in the case of cotton oil or castor oil the solidification resembles coagulation. In the case of red oil a thin film forms over the surface and apparently protects the under layer from further action until this film is removed. The oil when completely solidified is hard without any suggestion of tackiness. It is black and practically odorless. A highly refined edible corn oil when placed 4 inches from the lamp for 14 hours gave a jelly of a very light yellow color. The change of a fatty oil from a liquid to a solid state is very gradual, the oil becoming slightly viscous at first, then increasing gradually in viscosity until it finally assumes the jelly form. Immediately before the mass commences to solidify a large number of small bubbles usually appear beneath the surface of the oil and these may still be observed after the oil has become completely solid. (See page 180.)

Comparative Rapidity of Polymerization.

It is of interest that, although the gelatinized crude cottonseed oil was considerably lighter than the original crude product, the gelatinized refined oil as prepared above was much darker than the original refined oil. The average temperature of the oil during these experiments was 110°. It was noted that crude cottonseed oil, at relatively low temperatures, fumed slightly under the action of ultraviolet, while the refined oil did not give off any fumes until the temperature had reached about 160° C. Even at that point the fuming was only slight. The conclusion which may be drawn from these experiments and from some others carried out under practically the same conditions is that crude oil polymerizes and gelatinizes more rapidly than refined oil.

The question arose as to whether this gelatinizing effect was due to oxidation or mainly to the action of the rays themselves. In order to determine this, oil was placed in a tubular quartz container and the opening carefully sealed. The tube was then exposed to the action of ultraviolet for 5 hours at a distance of 4 inches from the lamp. At the end of this time the oil had become thickened so that it would no longer flow in the tube. The experiment was then repeated. This time the tube was filled completely with oil at the temperature at which the oil was to be exposed and the open end was carefully sealed. The tube was exposed to ultraviolet for 10 hours and at the end of this period the bubbles previously mentioned had begun to appear and the oil had become highly viscous. Thus, ultraviolet in the absence of oxygen is able to thicken and polymerize some fatty oils. In the presence of oxygen, however, the results of a number of tests indicate the solidification of unsaturated fatty oils under the influence of ultraviolet is due jointly to oxidation and polymerization.

In one case ordinary cottonseed oil was mixed with 5 per cent of sulphur and exposed to the action of ultraviolet for 3 hours at 150° C. and remained liquid after the treatment, but an oil which had been exposed until it was

practically at the gelatinization point and then had the same amount of sulphur added, on exposure in the same way yielded a black rubber-like solid.

In view of the results obtained with unsaturated fatty oils, a sample of oil which had been hydrogenated to a titre of 54° C., was exposed to ultraviolet in the same manner as the other oils, but for a period of 3 hours. At the end of this time practically no change was noted either in color, odor or viscosity. The stability of the oil under these drastic conditions was of interest.

In another case a mixture of equal parts of rosin and corn oil having the consistency of honey was exposed in a thin layer to the action of ultraviolet at a distance of 4 inches from the lamp. After 5 hours the product had become extremely viscous and was somewhat darkened. A longer exposure of another sample at a distance of 14 inches from the lamp gave a product of about the same consistency, although much lighter in color. The carbonizing or discoloring effect of exposure very close to the lamp was repeatedly noted. The discoloration may be due partly to the rays and partly to local superheating of the upper layers of oil.

In order to obtain an idea of how long an exposure is necessary to completely solidify the oil when exposed in a very thin film to ultraviolet, a layer of cotton oil about one-sixteenth of an inch in thickness was exposed at a distance of 4 inches from the lamp and the consistency noted every minute. The oil commenced to thicken almost immediately and at the end of 14 minutes had completely solidified to a very thick jelly. To determine whether thicker layers of oil were opaque to the ultraviolet rays, cottonseed oil was exposed at a distance of 4 inches from the lamp, the depth of oil in this instance being 1½ inches. After an exposure of 7½ hours it was found that the entire mass of oil had become solid and was nearly uniform throughout, the product being a dark colored jelly.

An interesting fact about some of the gelatinized products mentioned above is that on exposure to the air for about 24 hours they become opaque and quite brittle. If the product is tacky on removal from the burner, the surface closes its tackiness in a very short time. This drying progresses through the film until finally there forms a brittle mass which can be easily powdered.

Experiments on the oxidation and polymerization of soya bean oil have been carried out by *Taverne*.[39f] Oxidation in the air at room temperature was effected by Fahrion's method. The hydroxy acids of 3 grams of oil on 10 grams of cotton yarn were determined after thirty days' exposure and found to be 38.4 per cent. Oxidation at 70° was carried out in the apparatus of Genthe, and was complete in 30 hours. Oxidation in air at 150° was also carried out, according to Genthe, by heating in a beaker. The molecular weight rose in 10 days from 710 to 1730, a fact which indicated polymerization or condensation along with the oxidation. The oil became solid and contained 31.8 per cent hydroxy acids and 63 per cent fatty acids soluble in petroleum ether, while the iodine number decreased to 64.8. Genthe states that siccatives are inactive in ultraviolet rays, but Taverne, on the contrary, obtained complete oxidation in 45 hours. A lead manganese rosin compound containing 6.28 per cent lead and 5.76 per cent manganese was found to be the most active agent for hastening oxidation. On exposure to ultraviolet at 70° oxidation was complete with 5 per cent siccative in about 10 hours. (See page 180.)

Oil Hardening.

A process of hydrogenating oils involving exposure of the oils as a film on a web carrying catalytic material and at the same time exposing the oil and catalyzer to ultraviolet radiation has been proposed by Walter.[39g] One form of apparatus described by Walter for carrying out this reaction consists of a closed vessel in which is placed a belt or

[39f] Z. angew. Chem. 27, 1, 249, 1915.

[39g] Hydrogenation of Oils, New York, 1914, 34; Seifen. Ztg. 1913, 442. For negative results in attempting to harden oleic acid by ultraviolet see Curtis, page 180.

web carrying catalytic material. The belt may be made of asbestos or cotton cloth and may be impregnated with platinum, iridium, nickel or other catalytic material. The belt is carried on rollers, one of which dips into the oil. Catalyzers also may be carried in a container attached to the belt. The ultraviolet lamp is located in the closed vessel, thus irradiating the interior. Utescher [39h] treats oils with hydrogen in presence of a finely-divided catalytic agent, and at the same time the material is subjected to the action of a silent electric discharge.

Testing Hydrogenated Oils.

Ultraviolet rays may be used as a qualitative test in some cases for the detection of unhydrogenated oils in hydrogenated oils or fats. A well-hardened hydrogenated oil, such as hardened cottonseed oil of a melting point of about 60° C., is very resistant to the action of ultraviolet, while the cottonseed oil from which it is prepared is quite readily thickened by the effect of the ultraviolet radiation. Accordingly, a mixture of the two glycerides changes in appearance on exposure to ultraviolet. Many ordinary greases or fats such as soapmakers' tallows and the like are darkened and polymerized on such exposure, while hard fat of the melting point referred to is scarcely visibly changed. An exposure of several hours at a distance of 4 to 8 inches from the lamp is recommended.[39l]

Petroleum Oil.

As previously noted, petroleum oil may be treated by ultraviolet rays to destroy its bloom or fluorescence.[39j] Some oils, by exposure, are reddened in color or otherwise slightly darkened. Other oils are bleached by such treatment. Petroleum oils which are intended to be used as lubricants and which may have gumming properties due to unsaturated constituents, are improved in quality by exposure to ultraviolet radiation. Apparently polymerization occurs, resulting in the formation of saturated bodies. The oil may be exposed in an atmosphere of an inert gas. A high-voltage ultraviolet lamp is used advantageously and if the heat which emanates from such lamps is very considerable, the oil may be cooled during the exposure. Gray [39k] deblooms lubricating oil, paraffin wax and the like and brings about partial conversion to acids and esters by blowing air through the hydrocarbon material at 50-120° C., while exposing to ultraviolet radiation. Catalysts may be present and the operation may take place at pressures up to five atmospheres. Gray states that he has been able to convert 75 percent of the hydrocarbon material into fatty acids by this process. Continental Caoutchouc & Guttapercha Co.[39l] crack petroleum oils by heating in the presence of a catalyst and spraying through a zone irradiated with ultraviolet.

[39h] British patent 20,061, Sept. 3, 1912.
[39l] Ellis and Wells, Chemical Engineer, 1918, 221.
[39j] Ellis, U. S. patent 1,089,359, March 3, 1914.
[39k] U. S. Patent 1,158,205, Oct. 26, 1915.
[39l] French patent 469,948, Mar. 21, 1914.

Resins and Soaps.

Minor [39m] has employed ultraviolet for bleaching rosin. Cumaron resin [39n] is darkened on exposure to an ultraviolet lamp for three hours at a distance of a few inches. Ultraviolet rays render asphalt more insoluble.[39o] The solubility of colored resinates submitted to the action of light has been investigated by Larguier des Bancels.[39p] Colored resinates were prepared by treating resin with aqueous solutions of alkali hydroxides, adding a suitable coloring matter (safranine, rhodamine, etc.), and then precipitating with a salt of zinc or magnesium. These substances when dissolved in a volatile solvent, spread in a thin layer on glass plates, dried, and exposed to a mercury vapor lamp, became, at the end of a certain time, insoluble in such solvents as benzene, but soluble in solvents such as methyl or ethyl alcohol. The colloidal condition of stearates, palmitates and oleates of copper, aluminum, zinc, calcium and other water-insoluble soaps is affected adversely and solubility is impaired by ultraviolet radiation.[39q] A substitute for drying oils as a medium for paints, varnishes, and impregnating agents for fabrics, wood, etc., proposed by Rohm [39r] consists of a solution of polymerized acrylic acid ester, in acetone, lower fatty esters or other solvents. When exposed to sunlight or ultraviolet, the ester is stated to be transformed into a colorless, transparent, tough mass, which is soluble in solvents for oils.

Methods Involving Silent Electrical Discharge.

During the war a lubricating oil known as "Voltol" was said to have been produced in Germany from various thin oils by the action of the silent electric discharge.[40] The affinity of hydrogen for the unsaturated compounds existing in the oil, and very likely also a rearrangement of the oil molecules, are favored by glow discharges. These changes manifest themselves in the first place by a greatly increased viscosity.

The voltol process is carried out in closed cylindrical vessels arranged horizontally, each of about 30 cu.m. contents. The vessel contains a horizontal rotating shaft to which are attached four electrode holders. Each carries at its circumference a scooping gutter which during the rotating movement lifts the oil from the bottom of the vessel and pours it through the gap between the electrode plates, which are insulated from each other. These plates are built up of alternate layers of fibre and aluminium. The fibre plates constitute the dielectric medium and form opposite poles in constant alternation with each other. The glow discharges are produced by single-phase alternating current of from about 4,300 to 4,600 volts. However, the glow discharges will only commence after the pressure in the vessel has dropped to 0.9 atmosphere. This pressure must be maintained continuously inside the vessel by an air pump as

[39m] U. S. Patent 939,733, Nov. 9, 1909.
[39n] J. Ind. Eng. Chem. 1916, 800.
[39o] Gödrich, Monatsch. 1915, 36, 535.
[39p] Comp. rend., 1912, 155, 280; J. Chem. Soc. 1812, Abs. 102, ii, 882.
[39q] Jones, Chem. & Met. Eng., 1923, 28, 489; J.S.C.I. 1923, 42, 410A.
[39r] J.S.C.I., 1917, 296,, German patent 295,340, June 5, 1915.
[40] Engineering Progress 1922, 121.

otherwise the current, which should normally be between 19 and 23 amperes, will fall. Therefore the current is regulated by increasing or decreasing the pressure. In order to keep the oil from oxidizing it is treated with hydrogen gas. After a partial vacuum of 60 centimeters of mercury has been produced in the vessel, hydrogen is introduced for driving out the residues of air and oxygen. The pressure is then further reduced to about 65 millimeters of mercury by working the pump. In treating vegetable, animal, or mineral oils (which latter must be purified) the oil is heated to a temperature of 60° to 80°. The vessel is filled with hydrogen gas at 65 centimeters of mercury and the shaft with the electrodes and scoop is turned at a speed of one revolution per minute. The glow discharges between the various electrode plates soon convert the whole electrode body into a veritable cylinder of fire of a rose-violet color.

The property of "voltol" to remain comparatively fluid at low temperatures and very viscous at high ones, is said to render it very suitable for internal combustion engines, superheated steam cylinders, high-pressure compressors and heavily loaded ring-oiling bearings.

A catalytic process for obtaining chemical reaction between a gas and a liquid substance proposed by Slatineanu [41] is carried out in the presence of a "body" of metal, a part of which is immersed in the substance with which the gas is to enter into reaction, and the remaining portion projects or is kept free from the liquid and is exposed to the gas. The gas is subjected to the ionizing action of a silent electrical discharge, e.g., to rays of very short wave-length, such as ultraviolet rays, Roentgen rays or Lenard rays, whereby the particles of the gas are electrically charged and have a rapid movement imparted to them. The metal body under these circumstances is capable of occluding gas. In a modification of this process [42] the metal body is used as an electrode for a silent electrical discharge, the arrangement being such that the discharge is kept outside the substance which is to enter into reaction with the gas, so that the discharge acts upon the gas only and never directly upon the substance. The process is said to be capable of application in the hydrogenation of fats and of unsaturated hydrocarbons, reduction of alcohols, aldehydes, nitriles and nitro compounds.

Rubber.

Victor Henri is credited by Helbronner with being the first to expose rubber to ultraviolet rays, carrying out vulcanization with films made from solutions of rubber, as early as 1909-1910. Rubber solutions which have been vulcanized by means of ultraviolet, are stated by Helbronner [42a] to be insoluble in the same solvent when once they have been dried. Bernstein [42b] proposes vulcanizing rubber solutions containing sulphur by exposing them to the action of ultraviolet rays produced by a quartz mercury vapor lamp, the solution being spread on a moving metallic ribbon. A solution of rubber in benzene containing 6 per cent of rubber and sulphur equal to 10 per cent of the rubber when exposed in a film 0.5 mm. thick requires 40-50 seconds for vulcanization.

[41] British Patent 154,213, Nov. 22, 1920.
[42] British Patent 171,074, Dec. 16, 1920.
[42a] India Rubber World, Dec. 1, 1914, 130. Note also Compt. rend. 138, 1914, 1343 Chem. Zentr. 1914, 326; Koll. Zeit, 1913, 4; French patent 460,780 July 26, 1913.
[42b] British Patent 17,195, July 26, 1913; U. S. Patent, 1,240,116, Sept. 11, 1917.

Ordinary or high temperatures, pressure or vacuum, air or neutral gas atmosphere, may be used. During his experiments with different kinds of rubber Bernstein [42c] showed that the viscosity is diminished by heating, by mechanical working and by exposure to ultraviolet rays, and that if the depolymerization indicated by this reduced viscosity be carried to completion the final result is the same, whatever the agency employed—i. e., solutions of the depolymerized rubber of the same concentration show the same constant viscosity. With Frank and Marckwald's viscosimeter and using a 3 per cent solution of rubber in xylene the final constant viscosity value is 15 seconds. Depolymerization on heating takes place most rapidly between 60° and 85° C., according to the kind of rubber, and these temperature limits are close to the temperature above which, according to Spence, vulcanization occurs most actively. The vulcanization of rubber can be produced by exposing a xylene solution of rubber and sulphur to ultraviolet rays. A xylene solution of a mixture of Hevea plantation rubber with 6 per cent of sulphur was allowed to evaporate so as to leave a thin film on a transparent quartz plate. This was covered by another quartz plate and exposed on both sides for 40 minutes at a distance of 15 cm. to the rays from a Heræus lamp of 3 amperes and 110 volts. The film then possessed the properties of vulcanized rubber and contained 2.56 per cent of combined sulphur. Other experiments showed that the percentage of combined sulphur increased with the duration of exposure to the rays. The deterioration of vulcanized rubber on exposure to ultraviolet rays, observed by Henri, is considered to be chiefly due to "after-vulcanization." The tendency on exposure to ultraviolet of sulphur in solution is to polymerize it, converting it into an insoluble form. Stern,[42d] discussing the work of Bernstein, states that depolymerization occurs together with vulcanization. From Bernstein's observation that normal vulcanization of caoutchouc proceeds at ordinary temperatures under the action of ultraviolet, it is concluded by Ostromuislenski [42e] that, in absence of air, the rays activate sulphur by converting it into thiozone. The vulcanization is then effected partly by the latter and partly by the ozones formed simultaneously. According to Schopper [42f] solutions of coumarin derivatives—e.g., 1 per cent solution of dimethyl-amino-methylcoumarin—may be used to absorb the ultraviolet rays and hence protect the fabric of balloons from damage by sunlight. Jakowsky [42g] calls attention to the opaqueness of carbon black used as a reinforcing agent in rubber and notes the general belief that this property affords rubber of greater durability by preventing the penetration of light, especially ultraviolet rays, into rubber. The natural and arti-

[42c] J. Franklin Inst., 1913, 345. Note also Helbronner and Bernstein, Rubber Industry 1914, 156; Caoutchouc et Guttapercha 1915, *12*, 8720; J. S. C. I. 1915, 1105. Green, Ind. Eng. Chem. 1925, *17*, 802, has used the ultraviolet microscope in connection with a study of vulcanized latex globules.

[42d] Chem. Zeit., Rep. 1913.

[42e] J. Russ. Phys. Chem. Soc., 1915, 47, 1892-1898; J. S. C. I., 1916, 370.

[42f] Gummi-Zeit., 1915, 29, 1250; Z. angew. Chem., 1915, 28, Ref., 644; J. S. C. I., 1916, 356.

[42g] Bureau of Mines, Technical Paper 351, 1924.

ficial ageing of vulcanized rubber are compared by Pelizzola.[42h] Artificial (accelerated) ageing of vulcanized rubber is completely identical with natural ageing, from the chemical as well as from the physico-mechanical point of view. Accelerated ageing tests to control experimentally the behavior of definite mixtures under conditions of ageing are hence dependable. The action of ultraviolet rays upon crude and vulcanized rubber increases the oxidation.

Paper and Textiles.

According to Lewis[43] when an ultraviolet spectrum of wave-lengths 330 μμ to 210 μμ (3300 to 2100 Å) is projected on a sheet of notepaper or a piece of bleached cotton fabric, the spectrum becomes "degraded," i.e., the ultraviolet rays are converted into visible rays which can be photographed with an ordinary camera. Various papers and fabrics examined under these conditions give photographic images of varying intensities according to their composition and mode of manufacture. Acetylation of the cellulose greatly increases the fluorescence, but nitration depresses it almost to the vanishing point. The treatment to which cotton fabrics are submitted in bleaching as well as the degree of beating of pulp in paper-manufacture all find expression in the photographic images. It is possible that the method will be applied to the examination of analogous industrial products.

A method advocated by Dr. Wilbur L. Wright[43a] for waterproofing paper consists in impregnating the paper with a solution of gelatine, casein or similar proteid substance and bichromate of potassium or sodium. On exposure to the rays from a quartz mercury lamp the proteid material becomes insoluble and the paper is waterproofed while at the same time it is strengthened. The solution also may be added to paper pulp and exposure to ultraviolet carried out after sheeting.

Barr[44] notes that coarse yarns are less affected by light than fine yarns, as in the former the outer layers protect the inner ones. Weakening of cellulose threads by light appears to be due chiefly to rays of wave-lengths less than 400 μμ (4000 Å). The nature of the changes in cotton and linen produced by light are mainly due to oxidation. Silk is more affected by light than cotton, but wool is affected much less than either. Artificial silk is affected less than cotton. Rays from a quartz mercury lamp which weaken silk and artificial silk are almost entirely cut off by interposing a glass plate.

Waentig[45] tests the influence of light on textile fibres by determina-

[42h] Giorn. Chim. ind. applicata 1922, *4*, 458.
[43] J. Soc. Chem. Ind. 1922, *41*, 99 R.
[43a] U. S. Patent 1,542,539, June 16, 1925.
[44] Trans. Far. Soc. 1924.
[45] Z. angew. Chem. 1923, *36*, 357. See also J. Soc. Chem. Ind. 1920, *39*, 512 A; Vignon, ibid., 481 A; J. Soc. Chem. Ind. 1923, *42*, 825 A. Carver, Automotive Industries, 1924, 1011, recommends ultraviolet radiation as a means of testing the fabrics used in automobiles. Aston concludes that the deterioration of linen fabric under sunlight is due to ozone formed in or on the fiber. Report on the Action of Sunlight on Aeroplane Fabric, T 1019 Brit. Advisory Com. for Aeronautics, 1917.

tions of the tearing strength and elasticity. Wool is practically unaffected both by sunlight and by rays from a quartz mercury lamp, the washed fibres being slightly more sensitive than the raw wool. The exposed wool no longer gives the Allworden reaction.[46] Cellulosic fibres, in particular cotton, are more sensitive than wool to ultraviolet rays, the effect being eliminated by interposing a sheet of glass between the source of light and the fibres. Raw silk and acetate silk are also more sensitive than wool, while other artificial silks are but little the worse for exposure. Turner's hypothesis of photochemical oxidation is not supported by the investigator's experiments.

Meunier and Rey [47] have observed that neutral wool develops a rose-violet color when treated with the vapor or a solution of quinone, but a deep brown if previously exposed to sunlight or ultraviolet rays, and this sharp difference in color may be utilized for the production of photographic prints on woollen fabric. Wool has decreased activity towards quinone in proportion to its acidity, although after exposure to the ultraviolet rays acidic wool instantly becomes yellow when exposed to quinone. Wool bleached by means of sulfurous acid, and therefore acidic, instantly becomes yellow whether or not it has been previously exposed to ultraviolet rays; this reaction affords a useful test for wool bleached by means of sulfurous acid. Wool thus bleached and subsequently treated with a solution of sodium bicarbonate yields the usual rose-violet color with quinone. The influence of ultraviolet rays on the reactivity of wool towards quinone is not affected by the nature of the atmosphere surrounding the wool during exposure (ordinarily air may be replaced by nitrogen or carbon dioxide). Absolutely dry wool is not affected by quinone. A yellowish-orange color results when wool is immersed in neutral or alkaline solution of sodium nitrate for several hours at 100° C. and then air-dried, but no development of color occurs when a cold solution of sodium nitrate is similarly employed unless the impregnated wool is afterwards exposed to ultraviolet rays. This after-development of color by exposure to ultraviolet rays occurs less rapidly when acidic wool (e.g., wool bleached by means of sulfurous acid) is employed. Millon's reagent (a solution of mercury in nitric acid) imparts a color to wool, silk, and hair, only when it contains nitrous acid; the minimum amount of the latter essential for the development of color (red) being less for wool than for silk and hair. In the presence of a large amount of nitrous acid, a yellow color is instantly developed on wool, silk, and hair, and the red color is not observed. The superficial erosion of woolen cloth exposed to the air is ascribed by Heermann to ultraviolet rays.[48] The action is a photochemical one caused by light of 200-350 μμ (2000-3500 Å). The effects of dyes used by Heermann are probably due to the way they act as acceptors for impinging rays.

Palimpsests are photographed by Kogel [49] in the ordinary way with

[46] J. Soc. Chem. Ind. 1916, *35*, 416; 1917, *36*, 706.
[47] Rev. Gen. Mat. Col. 1924, *28*, 66.
[48] Chem. Ztg. 1924, *48*, 337.
[49] Sitzb. kgl. Preuss. Akad. Wiss. *37*, 1914, 97; Science Abstracts 24 A, 106.

the use of color-filters and with the aid of ultraviolet rays. When exposed to ultraviolet radiations of a quartz mercury lamp, the parchment fluoresces, but the erased writing remains almost dark, though the old inks used sometimes contained sulfur compounds; chemical alteration of the parchment, greasing, etc., generally does not weaken the contrasts. Thus fluorescence photography often brings out details not disclosed by the other methods and has much improved the exploration of old manuscripts.[50]

The use of ultraviolet rays in deciphering damaged documents is reported by Fonzes-Diacon, Faucon and Reynaud.[51] Chemical and photographic methods and X-rays were used without success to try to decipher a will which had remained some time in contact with a strong solution of sodium hydroxide. Heating for several hours at 110-120° C. brought out the writing to a slight extent, but not sufficiently to allow it to be read with certainty. On exposing the previously-heated paper to the action of a 220-volt mercury vapor lamp provided with a Wood screen the writing became fluorescent and could easily be read but not photographed. Janet [52] describes a method, due to Bayle and George, for distinguishing frauds in paintings. The canvas is exposed to the action of various rays, particularly the ultraviolet rays, and photographs are taken and enlarged. In this way it is claimed frauds can be detected.

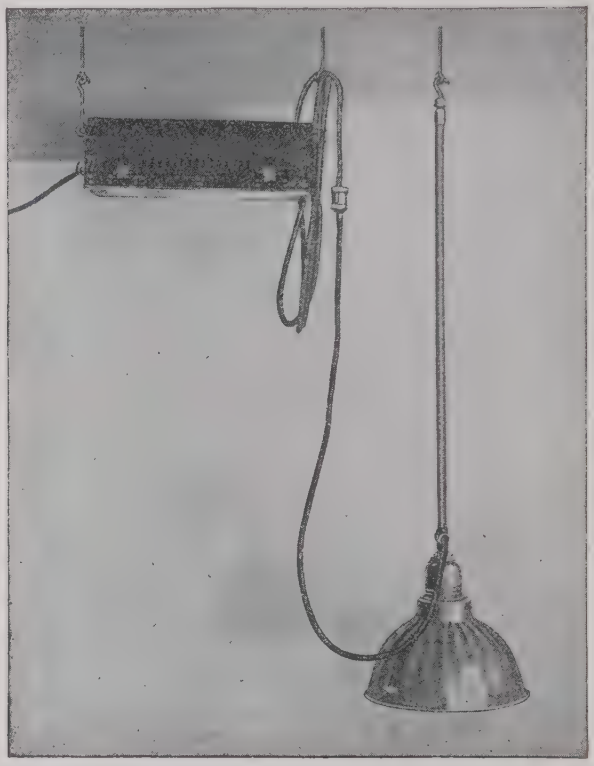
Food Products.

A method for the detection of shells in cocoa is described by Wasicky and Wimmer.[53] This method is based upon the difference in appearance between shell and nib tissue when viewed through microscope by ultraviolet rays. The proper irradiation is best obtained by means of a carbon-iron arc lamp, the light before reaching the mount being passed through a Wood-Lehmann filter (two blue uviol glass cells, one filled with 1:12000 nitrosodimethylaniline, and the other with concentrated copper sulphate solution). The color of the shell tissues when seen by the rays is buff or brown, the mucilage cells being almost colorless or a light yellowish green. The nib tissues appear in various shades of blue-violet.

Ultraviolet radiation also has been suggested in the treatment of flour with oxidizing agents. The process of the Naamlooze Vennootschap Industrielle Maatschappij Voorheen Noury and Van Der Lande employs a peroxide.[54] Flour or meal is mixed with a small quantity of an inorganic or organic peroxide and then subjected to a physical or chemical treatment to decompose the peroxide. One procedure is to pass bolted flour (mixed with 0.7 per cent of a solution of hydrogen peroxide of 3 per cent strength) in a layer three centimeters thick on a belt conveyer, through a chamber in which mercury vapor lamps are

[50] Hartley, Chem. Ztg. 1909, *33*, 586, recommends metastyrol for use in photomicroscopy as an immersion liquid for lenses of uviol or quartz.
[51] Ann. fals. 1924, *17*, 20.
[52] Chem. & Ind. 1924, *43*, 67.
[53] Z. Nahr. Genussm. 1915, *30*, 25.
[54] British Patent 102,967, Dec. 22, 1915; Chem. Abs. 1917, *11*, 1219.

situated.[55] A modified form of this procedure is that advocated by Sutherland.[56] Meal or flour is treated with sufficient chlorine to react upon the enzymes present and render them inactive and is then treated with hydrogen peroxide and exposed to ultraviolet rays to liberate oxygen which acts as a bleaching agent. Sutherland [57] also claims that meal, flour, cereals, beans or tubers are improved in color and baking



Courtesy Cooper-Hewitt Electric Company.

FIG. 84.

qualities by treatment with hydrogen peroxide and then exposing in a thin layer on a traveling belt conveyer to the action of the rays. A somewhat similar process is advanced by Gelissen.[58]

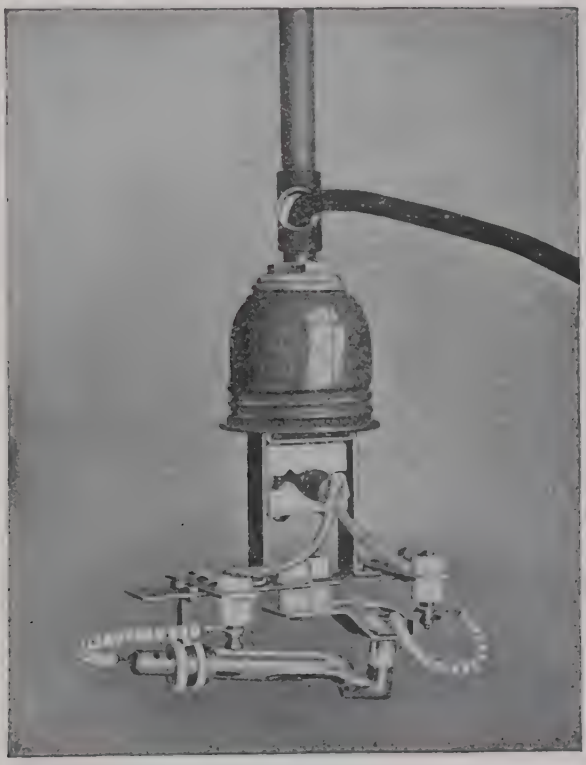
[55] In the laboratory of the senior author samples of low-grade flour or middlings have been considerably bleached after an exposure of 8 hours at about 6 inches from a mercury vapor lamp. The change is too slow to offer commercial possibilities.

[56] U. S. Patent 1,381,079, June 7, 1921.

[57] U. S. Patent 1,380,334, May 31, 1921. In U. S. Patent 1,539,701 the addition of benzoyl peroxide is recommended.

[58] U. S. Patent 1,483,546, Feb. 12, 1924.

Flour either after or preferably during the milling process may be treated with a substance of the paraldehyde-ozonide class. The effects may be enhanced in some instances by intensive milling, use of ultraviolet rays or of steam or warm water. Preferably the catalase and similarly acting enzymes in the material are destroyed, e.g., by the use of a very small amount of chlorine insufficient to bleach the flour, in order to permit the fuller action of peroxidase in liberating nascent oxygen in contact with flour material. Among the compounds which may be used are paraldehyde-ozonides, perozonides, peroxozonides, ozonide peroxides or polymers of the ozonides and similar compounds.



Courtesy Cooper Hewitt Electric Company.

FIG. 85.

A curious application of ultraviolet radiation is in poultry houses for the prevention of rickets in chickens, and the consequent loss in egg production.[59] A daily exposure of a definite period is prescribed. A specially designed treating apparatus using a quartz mercury arc is shown in Figures 84 and 85.[60]

[59] Contrib. No. 107, Department of Chemistry, and No. 27, Department of Poultry Husbandry, Kansas State Agr. Sta. Hughes, Nitcher and Titus report that the action of ultraviolet in preventing rickets in chickens is due to direct action and not to any changes in the room air. J. Biol. Chem. 1925, *63*, 205; Chem. Abs. 1925, *19*, 2068.

[60] Cooper Hewitt Elec. Company.

Minerals and Metals.

Turning from such materials as dyes, oils, flour and the like, we find among mineral substances a prolific field of study and one which never fails to interest the amateur experimenter in ultraviolet radiation. The degree of fluorescence of some materials is surprising to those who first view the effect of the radiation. Baskerville[61] notes the importance of ultraviolet in testing of minerals. The differences in color of the fluorescence affords a rough means of identification in some cases. A simple spark apparatus can be used in such experiments and tests. Certain minerals are inert, others fluorescent, some phosphorescent. Kunzite was discovered by aid of ultraviolet rays. A large number of spodumane samples were tested and all found to be inert except one. Upon closer examination this one was found to contain a hitherto unknown mineral which was named Kunzite in honor of the discoverer, Dr. Geo. F. Kunz. All the minerals from Mono Lake are phosphorescent after treatment with ultraviolet. Some of the same minerals from other localities are not phosphorescent. The genuineness of diamonds may be proven by their phosphorescence after being subjected to ultraviolet rays. The purity of tailings or precipitates may be tested and minerals sorted. A crushed mineral may readily be separated into a fluorescent and non-fluorescent portion by sorting while acted upon by ultraviolet rays. This principle is said to be utilized by the New Jersey Zinc Co. for testing willemite concentrates and tailings. The willemite is fluorescent while the gangue is inert. If the tailings contain no fluorescent specks it shows that the concentrating tables are working well. The eye can thus roughly judge the character of the concentrates.[62]

That exposure of a polished metal surface to ultraviolet rays may render it increasingly liable to corrosion is indicated by tests conducted by the Bureau of Standards, Department of Commerce.[63] Specimens of Armco iron, medium carbon steel, stainless steel, and high nickel steel were used for the tests and were exposed to the rays for 8 hours. Moisture from the breath was found to condense differently on the exposed and unexposed surfaces, rendering the two easy to distinguish. On the exposed part the drops of condensation were larger than on the unexposed, and the surface looked as if a very thin film of oil had been spread over it, making it less easily wetted than is the unexposed surface. In case of medium carbon steels very noticeable corrosion of the exposed spot was found to occur after four condensations of moisture, while the rest of the surface was hardly attacked. Chromium and nickel steels did not show any corrosion, although there was the same difference in appearance between exposed and unexposed surfaces.

It is of interest to note that Miethe has reported[64] the finding of small amounts of gold from the decomposition of mercury, through the

[61] Electrochem. & Met. Ind. 1906, *4*, 435.
[62] Note Andrews spark apparatus illustrated in Chapter 2.
[63] Ind. & Eng. Chem. 1924, *2*, 7.
[64] Naturwissenschaften 1924, *12*, 597; Chem. Abs. *18*, 3139.

operation of a new type of mercury vapor lamp, with very high energy input.[65] Gold was not found present in the mercury used, nor in the electrical connections, according to these reports. Nagaoka[66] also is reported to have obtained gold from mercury, using a mercury lamp, the anode of which was exposed in air, operating at 226 volts. Kaul[67] attributes the conversion of mercury into gold[68] to the loosening effect of the ultraviolet rays on the hydrogen atoms in the mercury atom, which is regarded as built up of hydrogen, helium, and carbon atoms. The hydrogen atoms are unable to resume their place in the system when the ultraviolet radiation is withdrawn, and by the removal of four hydrogen atoms the gold atom is formed. The transformation of mercury into gold in the mercury vapor lamp as noted by Miethe[69] is explained by von Antropoff[70] on the assumption that one or more isotopes of mercury, which must be isobaric with one or more isotopes of gold, undergoes the addition of one electron to the kernel. The transmutation Gaschler[71] claims can be obtained by so overloading a mercury lamp that it is fortunate if the tube is not destroyed. X-radiation of the vapor is also helpful. Gaschler's explanation is that several electrons are first stripped from the atom under favorable conditions followed by the loss of a proton from the nucleus, whereby the atomic number is reduced from 80 to 79.

Lighting by luminous paints is proposed by Risler.[72] A surface coated with a luminous paint containing a phosphorescent sulfide is rendered continuously luminous by subjecting it to the rays of the spectrum ranging from blue to ultraviolet. To obtain the rays, a vacuum tube activated by high-frequency current and filled with rarefied gas such as nitrogen, argon or air is preferably used. The degree of vacuum may be 4-10 millimeters of mercury. In a modification of the process by Risler,[73] a vacuum tube with or without electrodes and filled with rarefied gas such as argon, nitrogen or air is coated internally or externally with a luminous paint containing a phosphorescent sulfide, or having the sulfide incorporated in the glass of the tube, whereby a continuous luminous effect is obtained. The sulfide may be mixed with a varnish and the luminous coating is preferably covered with an impermeable and fireproof coating comprising cellulose acetate, alcohol triacetin, acetone and tetrachloroethane.

[65] See Chem. Age, London, 1924, *11*, 136.
[66] Ind. & Eng. Chem. News Ed. 1925, *3*, No. 2.
[67] Metallbörse, *14*, 1432; from Chem. Zentr. 1924, ii, 1049.
[68] Miethe and Stammreich, Naturwiss., *12*, 597. Chem. Abs. 1924, *18*, 597. Since the potential gradient in the Heraeus high-pressure lamp is slightly greater than in the Jaenicke lamp, conditions in the former, according to Retschinsky, are more favorable for the penetration of the atomic nuclei by electrons. Slightly modified Heraeus lamps have been constructed to work at a potential gradient of 21 volts/cm. and 150 cm. mercury pressure. Physikal. Z. 1925, *26*, 280.
[69] Chem. Abs. 1924, *18*, 3139.
[70] Z. angew. Chem. 1924, *37*, 827.
[71] Z. angew. Chem. 1925, *38*, 127.
[72] British Patent 207,786 of 1923.
[73] British Patent 208,723, Dec. 20, 1923.

Miscellaneous Tests.

Ultraviolet rays are employed by Castille and Henri[74] to test the purity of organic solvents. The results are obtained by studying the absorption spectra in the ultraviolet. Foyer[75] discusses the utility of ultraviolet spectrograms made with the Fery's spectrograph, in connection with the identification of essential oils. It is well known that good quality peppermint oil when used as a flavoring for certain candies or sugar preparations, such as ordinary mint tablets, loses its fine flavor on long standing. In the laboratory of the senior author a number of samples of mint tablets were exposed to the action of ultraviolet in order to test the stability of certain mint oils in the manufacture of confections. It was found that a few hours' exposure to the rays afforded approximately the same ageing effect as standing on the shelves for a period of several months. The procedure appears to be a ready method of testing materials of this class to quickly determine their keeping qualities.

Andrews[76] proposes a method of determining whether the lenses of ordinary spectacles or eyeglasses are of the proper material to protect the eyes, the test being to insert the lens between the source of light and a substance which shows fluorescence. If the fluorescence continues the lens is not impervious to ultraviolet rays. See Chapter 4.

Bayle and Fabre[77] note that the fluorescence observed in certain compounds under the influence of ultraviolet light from a mercury lamp affords a means of separating mixtures (e.g., novocaine and stovaine) and of detecting the presence of impurities (e.g., salicylic acid in milk). The fluorescence induced by light of 3650 Å., in various dihydric phenols, derivatives of benzoic and hydroxybenzoic acids, and other compounds (e.g., novocaine, saccharin) is a property which should not be overlooked.

In order that photo-electric photometry may be successful, a method more accurate than visual color matching must be available for determining the color of a light source. Such a method can be based on the comparison of currents excited by the source in two photo-electric cells of different frequency sensitivity characteristics. Cells filled with rubidium and sodium respectively were found to be suitable for this purpose. An apparatus designed to embody these conditions and capable of detecting a change of 0.5° in the temperature of the source at 2400° (abs) has been devised.[78]

[74] Bull. Soc. Chim. Biol. 1924, *6*, 299.
[75] Am. Perfumer 1922, *17*, 309.
[76] Gen. Elec. Rev. 1916, 317.
[77] J. Pharm. Chim. 1924, 535. See also ibid. 1925, 248. Dietzel and Taufel, Z. Nahr. Genussm. 1925, *49*, 65, test lactic acid, also saccharin in this manner. In the rays of a Wood mercury vapor lamp, Frehse, Ann. fals. 1925, *18*, 204, observed refined olive oil to possess a bluish green fluorescence, while the raw oil gave an orange fluorescence.
[78] Campbell and Gardiner, J. Sci. Instr. 1925, *2*, 177.

ADDENDA.

In studying the action of ultraviolet rays on egg-albumin in relation to the isoelectric point, Clark [79] observes that with solutions of egg-albumin of p_H 4.8, ultraviolet causes aggregation and flocculation; otherwise an increase in dispersion results. Changes in charge are accompanied by change in chemical properties. As the p_H becomes less than 4.8, the precipitation on half-saturation with ammonium sulfate increases. Positively but not negatively charged particles of albumin are precipitated by sulfate-ions.

The effect of different salts or the degree of dispersion of organic colloidal solutions, such as egg albumin, taka-diastase, blood-serum, and lettuce juice, was examined by Tadokoro [80] by observing the changes induced in their absorption spectra in the ultraviolet. Certain pairs of salts were shown to have antagonistic effects on dispersion. Scott and Svedberg [81] have made studies on the mobility of egg albumin, taking advantage of the fluorescence of the protein when subjected to ultraviolet radiation to determine the position of the protein layer in the U-tube employed. The apparatus was constructed of Pyrex glass, and quartz mercury lamps were used.

Dede and Walther [82] obtained colloidal solutions of arsenic by bubbling purified arsine through water which is exposed to light of short wave-lengths. According to the dilution, these solutions are yellow to bluish-violet in color. Only the most concentrated solutions show any tendency towards coagulation; more dilute solutions slowly become colorless owing to the gradual oxidation of arsenic to arsenious oxide. They are very insensitive towards electrolytes. The particles are negatively charged. The behavior of the solutions towards ammoniacal silver solution, mercuric chloride, and alkaline copper solution proves the particles to be arsenic and not solid arsenic hydride.

Solutions of metals in water and organic media, prepared by Schaum and Friederich [83] according to the methods of Bredig and Svedberg, and of sulfur and arsenious sulfide in water, and suspensions of anthracene in pure hexane showed no difference in the migration velocity in ultraviolet rays and in light of long wave-length. Zinc hydrosol alone showed a small decrease in the velocity on exposure to ultraviolet radiation. The effect was not observed with zinc solutions in alcohol, and is probably due to some chemical action. Electrophoresis of hydrosols of the silver halides is appreciably affected by light, which can bring about reversal of the direction of migration. The presence of silver oxide particles in a silver solution in water prepared by Bredig's method can be investigated by adding gelatine and observing a thin preparation in

[79] Amer. J. Hyg. 1922, *2*, 322; cf. Amer. J. Physiol. 1922, *61*, 72.
[80] J. Coll. Agric. Hokkaido Imp. Univ. 1921, *10*, 37.
[81] J. Am. Chem. Soc. 1924, *46*, 2700; see also Svedberg and Jette, ibid., 1923, *45*, 954.
[82] Ber. 1925, *58*, B 99.
[83] Z. Wiss. Phot. 1924, *23*, 98.

the microscope with dark ground illumination. If acetic acid is allowed to diffuse in, any silver oxide particles are rapidly dissolved.

Blair [84] points out that the age of gels has a great influence on the formation of Liesegang rings. The distance (a_∞) to the last ring formed increases regularly from zero age to about 10 days. With gels older than this, ring formation ceases. Either intense white light or complete darkness causes irregular ring formation and a decrease in a_∞. Diminution of a_∞ is greater for blue than red light of the same intensity. The action of any visible light is irreversible in the sense that reliquefaction and resetting do not relieve the anomalous setting. Ultraviolet from a quartz mercury lamp in a few hours renders a gel incapable of Liesegang-ring formation. The effect of ultraviolet, unlike that of visible light, does not persist.

With reference to the action of ultraviolet in producing fog nuclei see Ransauer.[85] On the formation of nuclei in moist air see Wilson,[86] also Saltmarsh.[87] The nuclei are equally effective in producing condensation of water, toluene, and turpentine vapors, and they are formed even by rays which have traversed 50 centimeters of air. Alcohol vapor condenses without expansion on much smaller nuclei than water. No nuclei are formed by radiation in absence of oxygen or carbon dioxide. It seems probable that the nuclei formed by ultraviolet do not cause condensation by virtue of any particular chemical change, but that they are particles large enough to act, like dust particles, as centers around which condensation can begin.[88]

Beer Söhne [89] advocates a process in which alkaline suspensions or emulsions of certain carbon products [90] are mixed with a solution of precipitated silver oxide, mercuric oxide, auric oxide, or copper oxide in dilute formic acid, excess of acid being avoided. The whole is well shaken and allowed to stand in daylight or ultraviolet rays for some hours, by which time the metal absorbed on the carbon products has been completely reduced. By addition of dilute alkali the precipitated colloid is again dispersed together with the absorbed metal. Instead of using formic acid, the freshly precipitated metal oxides or hydroxides may be shaken with the alkaline colloidal solution. The solutions obtained are claimed to have therapeutic value. In an electrolytic process for the separation of platinum from other metals contained in platiniferous materials Slatineanu [91] advocates the electrolysis of an aqua regia solution containing the mixed metals, which is carried on until a limit of 3 per cent for gold, 6 per cent for platinum, and 0.5 per cent for palladium in the solution is reached, whereby only gold is precipitated from the solution. Gold and palladium are then reduced by passing hydrogen, previously submitted to ultraviolet rays, into the solution. A voltaic couple may be introduced to assist the reduction. Platinum may be separated from the resulting solution by electrolytic means, and if the anode is exposed to the influence of ultraviolet radiation, chlorine combines with the hydrogen atoms of the water and the liberated oxygen oxidizes nitrogen oxides to nitric acid and so renders possible a complete cycle of operations. The apparatus consists of tanks in which the various stages of the reactions occur, the whole being connected to form a closed circuit.

[84] Phil. Mag. 1925, *49*, 90.
[85] Ber. Deut. Physikal. Ges., 1911, *13*, 899; J. Chem. Soc. 1912, *102*, ii, 5.
[86] Proc. Roy. Soc. London, 1898, *64*, 128.
[87] Proc. Phys. Soc. London, 1915, *27*, 357.
[88] Note also Audubert, Ann. phys. 1922, *18*, 5; Chem. Abs. 1922, *16*, 3812, in reference to the action of ultraviolet on suspensions of sulphur and also of gum mastic. Light of short wave-length speeds the growth of the particles.
[89] German Patent 381,270, Aug. 18, 1918.
[90] German Patent 337,410; Ber. 1924, *48*, 45.
[91] British Patent 157,785, Jan. 10, 1921; J. Soc. Chem. Ind. 1922, *41*, 470 A.

An examination by Schaum and Friederich[92] of the electrophoretic migration velocities of several hydro- and organo-sols of various metals under the simultaneous action of visible and ultraviolet rays failed to detect any systematic change. Only with zinc hydrosol was a slight decrease in the velocity of drift detected. Hence any possible photoelectric effect on the particles exerts only a negligible influence on the velocity of drift.

Changes in the magnetic permeability of the silver halides due to the action of light Garrison[93] concludes is probably a result of changes in electric polarity within the molecules. The diamagnetism of silver chloride was reduced and the paramagnetism of silver bromide and silver iodide increased by exposure of the salts to radiation from a tungsten lamp. Removal of a water cell which absorbed the heat rays of the lamp produced an increased effect.

Manganese chloride solution (10 per cent) is reported by Rousseau to have the power of "photocatalytic resonance" which it preserves for many months. This power seems to increase with ultraviolet rays, but diminishes with the prolongation of the irradiation. The quality and not the intensity of the vibratory frequency apparently determine the amount of ultraviolet energy fixed by the manganese chloride, since with 3600 candle power lamps the action is not triple that of a 1200 candle power lamp but only double.[94]

The quantity of ultraviolet energy required to render developable a grain of photographic silver bromide is reported by Helmick[95] as follows. For 2537 Å., the average quanta per grain is 731 ± 14, for 2653 Å., 514 ± 11, for 3131 Å., 510 ± 16, for 3650 Å., 555 ± 13. Thus small energies are more efficient in producing developable grains than large energies. The results of determinations of the absorption of the silver bromide and the gelatine in an ordinary photographic emulsion are given by Helmick.

Zolcinski[96] reaches the conclusion that chemical nitrification of ammoniacal solutions of natural or artificial humus substances can take place in the sunlight, but not in the dark. The process is more rapid in quartz vessels than in glass vessels, and is accelerated by the addition of artificial humus substances, or of aluminum hydroxide calcined at 210°-220° C.

Coblentz and Fulton[97] atomized suspensions of B. coli over the surface of hardened sterile beef-peptone agar in a Petri dish, and exposed to ultraviolet radiation from a quartz mercury arc lamp; the radiation being filtered through screens of mica, which is found to have a well-defined absorption band at about 260 μμ. Previous exposure of the agar had no effect, although with very high radiation intensities subsequent growth was inhibited. Germicidal action extends up to 365 μμ, decreasing with increasing wave-length; very prolonged exposure is required from 297 to 365 μμ. The lethal action of waves below 280 μμ is at least 10 times more rapid than that of waves beyond 305 μμ, in spite of the much lower intensity of the shorter waves. Intermittent exposure has the same effect as continuous exposure for the same time of radiation, *i.e.*, the action is cumulative. The energy between wave-lengths 170 and 280 μμ required to kill a bacterium is about 19×10^{-12} watt.

[92] Z. wiss. Phot. 1924, *23*, 98.
[93] J. Am. Chem. Soc. 1925, *47*, 622.
[94] Compt. rend. soc. biol. 1924, *91*, 1190. British Patent 226,534, Dec. 17, 1923.
[95] J. Opt. Soc. Amer. 1924, *9*, 521.
[96] Rocz. Nauk Rolniczych 1923, *10*, 311; Chem. Zentr. 1925, *96*, I, 1123.
[97] U. S. Bur. Standards, Sci. Paper 495, see also ibid. Nos. 330 and 378.

A procedure advocated by Marie and Raleigh [98] for the polychromization of methylene blue consists in dissolving 1 gram methylene blue in 100 c.c. of aqueous 0.5 per cent sodium bicarbonate and exposing in an open shallow dish to an arc lamp for 10 to 30 minutes. When the mixture is cool slowly add 500 c.c. of 0.1 per cent yellowish eosin solution until the solution becomes purplish with a metallic luster on the surface, in which a fine black powder is formed. Filter, air-dry, and dissolve 0.1 gram in 60 c.c. of acetone free from methyl alcohol.

Schroeter [99] discusses the present importance of electroluminescence lamps, of their internal processes in the light of recent theories of atomic structure, and of the possible development of this type of lamp, especially in regard to efficiency.

Piutti [100] states that carbon electrodes which have been alternately heated to redness and immersed in ferric chloride solution a few times may be employed with advantage instead of iron electrodes for generating ultraviolet.

[98] J. Lab. Clin. Med. 1924, *10*, 250.
[99] Elektrotechnik u. Maschinenbau *38*, 1920, 237-42, 251-7.
[100] Atti. R. Accad. Lincei, 1913, (v) *22*, ii, 92; J. Chem. Soc. 1913, *104*, ii, 896.

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